Department of Chemical Engineering

National Institute of Technology Rourkela

December 19, 2016

Certificate of Examination

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We the below signed, after checking the dissertation mentioned above and the official record book(s) of the student, hereby state our approval of the dissertation submitted in partial fulfilment of the requirements of the degree of *M.Tech (Research)* in *Chemical Engineering* at *National Institute of Technology Rourkela*. We are satisfied with the volume, quality, correctness, and originality of the work.

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This is to certify that the work presented in the dissertation entitled "Preparation and characterization of Cassia-4 Hydroxy-benzoic acid resin for removal of Cr^{+6} from contaminated water" submitted by Shreeparna Mishra, Roll Number 614CH3003, is a record of original research carried out by her under my supervision and guidance in partial fulfillment of the requirements of the degree of M.Tech (Research) in Chemical Engineering. Neither this dissertation nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

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Dedication

This thesis is dedicated to my parents; the reason of what I become today, thanks for your continuous support and intensive care, this honorable work is a symbol of my love and respect towards you.

Shreeparna Mishra

Declaration of Originality

I, Shreeparna Mishra, Roll Number 614CH3003, hereby declare that this dissertation entitled “Preparation and characterization of Cassia-4 Hydroxy-benzoic acid resin for removal of Cr^{+6} from contaminated water” presents my original work carried out as a M.Tech (Research) student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section “Reference”. I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

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Acknowledgment

I sincerely thank my supervisor, Prof. Susmita Mishra for guiding me into this research field and for their constant help, encouragement, and endless support on my research work. Her care and enlightenment strengthened me in every progress of this work.

I would like to express my profound gratitude to my D.S.C members Prof. Abanti Sahoo, Prof. Arvind Kumar, Prof. Aditya Kumar, and Prof.Sudipta Sen for their valuable suggestions in several occasions during my research work. I would like to acknowledge the department of Chemical Engineering, National Institute of Technology (NIT), Rourkela for providing me various facilities throughout my research work.

During my M.Tech.(Research) work, I am very much grateful to my friends especially Krutika Lokapriya Routray, Shilpi Das, Pallavi Suhashinee Behera , Suresh Sir, Harinandan Kumar for their kind care, selfless help, and the deep friendship.

Finally, I wish to express my hearted appreciation to my family. Their deep love, understanding, constant support and encouragement over the years are the great impetus to my research.

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Abstract

The current research emphasizes on removal of Cr^{+6} from the contaminated water by the preparation of natural resin using cassia gum powder and testing its feasibility to reduce Cr^{+6}in contaminated water. The effects of various process parameters including pH of the solution, amount of resin, initial Cr^{+6} concentration, contact time etc., on removal efficiency of Cr^{+6} from the water stream has been studied. The study demonstrates that the prepared natural CHBA resin has potential to remediate $Cr+^{6}$ from the drinking water. It is observed that using 1g/ml resin 99.26% Cr^{+6} could be removed from initial concentration 3 ppm at pH 6.8 within 25 min. Experimental data obtained were allowed to fit to various models such as pseudo first order model, pseudo second order, intra particle diffusion, Elovich model. Results indicate that the process of adsorption on Cr^{+6} was followed by second order kinetic model with R^2 value 0.989.Similarly other models of adsorption isotherms such as Langmuir, Freundlich, Temkin were also applied to the data and constants of isotherms were calculated. Cr^{+6} adsorption on the prepared resin shows good agreement to Freundlich adsorption isotherm model with the regression coefficient of 0.989. Thermodynamics parameter studied that the Positive values of change in enthalpy shows that there is a presence of an energy barrier during the process of adsorption and the process of adsorption follows process of endothermic reaction. The positive values in the change of entropy (ΔS) shows good binding capacity of Cr^{+6} ions for the resin surface and it also increases the uncertainty of the solid solution interaction during the process of adsorption.

RSM experiments were also conducted which showed that the ideal conditions required for Cr^{+6} adsorption were as per the following: amount of resin as (0.43 g), at pH (6.13) as well as Initial Concentration of (4.53 mg/L) with the value of maximum adsorption is 95.05%. The following results were obtained from the box-behenkn design RSM method with a desirability of 0.989. The Column performances were also evaluated by varying the amount of resin inside the column bed, influent rate of flow with Cr^{+6} concentrations. Furthermore it was seen that with the expansion in height or depth of the bed, at lower flow rates and at low Cr^{+6}concentration the column performance was good or proved to be better.

Keywords: Resin, Cr^{+6} removal, wastewater treatment, adsorption

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Chapter 1

INTRODUCTION

Disposal of industrial effluent contaminated with heavy metals typically $Cr^{+6}$is a serious environmental issue as it ultimately gain access to surface and ground water which may be used for drinking purpose. This pollutant is released into the water bodies by discharges from textile industries, industries of leather tanning, electroplating as well as metal finishing. It also causes detrimental effects at a point when its respective concentration of 0.1 mg/g is achieved by the body and has been considered as lethal **[1]**. Hence various regulatory bodies have enforced strict regulation for discharge of cr^{+6} to the water bodies and its permissible limit has been stated as 0.05 ppm **[2].**

Thus to mitigate these pollutant released into the water bodies various techniques have been adopted which includes coagulation, flocculation, electrolytic reduction, biodegradation etc. The greater part of these techniques experiences the ill effects of certain demerits like high sludge production, handling and disposal problem, slow process etc. Membrane separation process is yet another method adopted to remove $cr^{+6}$from the waste stream that works at high pressure, is quite expensive and is incapable to treat larger volumes of waste water. However adsorption using various adsorbents has been widely used by the researchers. Various low cost natural adsorbents such as activated charcoal, wheat grain, activated neem leaf powder prepared from activated carbon and groundnut shell powder, Orange Peel, Avena monida (oat), sawdust, rice husk, Papaya wood , maize leaf, modified sawdust of walnut, cocoa shells, have been successfully used by authors to reduce $Cr^{+6}$from the waste water **[3,4,5,6,7,8]**. Many researchers have worked with activated carbon and have successfully reduced Cr^{+6} to permissible limits. All these adsorbents has a major demerit as it requires regeneration, results in loss of adsorbents and is limited to applications for Cr^{+6} removal at low pH(<2) **[9]**. Hence resins have been a good alternative to reduce Cr^{+6}.It possess great mechanical properties, good imperviousness to ecological degradation, great glue like properties, low shielding properties ,low shrinkage, easy and quick curing etc. It has been used extensively to treat drinking water due to its important properties such as applicability at neutral pH and capability to treat low concentration of pollutant.

The resins are categorized commonly into two types which can be utilized to detoxify polluted water as in the form of synthetic and natural resin. The hydrophobic nature can only be seen with the resins which are prepared from divinyl benzene-styrene **[10].** Resins which are synthesized mainly from products of petrochemicals, are quite expensive. The two important parameters like the functional groups residing in the resin as well as pH of the respective solution is totally dependent on their capacity of Ion-exchange .Thiol, thiourea, dithionite, aspartate and triisobutyl phosphine sulfide are the widely used functional groups which are effectively used for different metal ions removals **[11, 12, 13, 14, 15]**. Some of the important properties of Ion exchange resins are they are hydrophobic in nature and are non-biodegradable. This is because of the reason of the expansion in the costs of petrochemical items so that Natural man-made materials could be used instead of this ion exchange resins. Tamarind kernel powder, Guar gum Powder, Xanthium gum powder, Sesbania gum powder etc. **[16]** are extensively used natural products which have been employed for the treatment of waste water by removing several metal ions Such materials are biodegradable as well as are less costly. A few metals holds resins consisting of a series of complexing or chelating lignin's that have been accounted to adequately remove overwhelming metal ions **[17] .** Several groups like Amino, thio, Oxo, carboxyl, phosphoryl, has been already proposed and established. Among these groups, amino/carboxyl group can provide highest adsorption of metals **[18, 19].** Later on, it was proposed that amino group can accommodate large number of vacant sites for the process of adsorption to occur **[20]**.

Henceforth an effective sorbent with high limit and high rate of adsorption requires higher area around the surface of the adsorbent **[21]**. Due to the increment in contamination level in the water, these types of new materials are thus being employed. Thus Cassia gum powder, a characteristic material which can be found through the seeds of endosperm of Cassia tora and cassia obtusifolia that has a place in leguminosae family has been utilized to synthesize natural resin. This tree is generally developed in tropical area and has high therapeutic quality.

Optimization of process parameter on adsorption of Cr^{+6} on the resin has been reported by many authors **[22]** has demonstrated experiment on adsorption of Cr^{+6} using Lewatit FO36 ion-exchange resin by varying pH from 5.0–8.0 and reported adsorption of maximum capacity when the pH is adjusted to 6.0. Influence of adsorbent dosage has been identified utilizing resins containing cationic exchange like IRN77 and SKN1 and As the resin amount was increased from 0.050 to 0.1g shows change in adsorption behavior of Cr^{+6} **[23]**. Contact time plays a major role in the effective Cr^{+6} adsorption on resin as reported by various authors **[24]**. The time after which there is no further adsorption of Cr^{+6} on the resin was attained at 30 min and that time is known as the equilibrium time. Similarly influence of Cr^{+6} concentrations affected the Percentage removal. It was found the highest removal of 99.4% of the removal was obtained by keeping the process parameters at initial concentration of 100ppm **[25]**. Cr^{+6} adsorption data has been verified by established isotherms such as Freundlich, Langmuir, Temkin, D-R models **[26].**

Thus this research reports the feasibility of removal of Cr^{+6} ions from water using cassia gum powder resin. Various process parameters such as amount of resin, effect of time, effect of pH, effect of Cr^{+6} concentration has been studied to test the removal of Cr^{+6} by the prepared CHBA resin using batch experiments . Column study to explore its design parameters has been also studied. Various model equations has been used to fit the experimental data too.

ORGANIZATION OF THESIS:

Chapter 1 consists of introduction to Cr^{+6} and its toxicity, properties, sources of release, its permissible limits and remediation methods. Use of resins for Cr^{+6} removals by various researchers and advantage of using natural resins has been discussed in brief. It highlights the optimization of process parameters to effectively reduce Cr^{+6} from the waste water.

Chapter 2 includes Literature Review which describes the toxicity of Cr^{+6}, the permissible limits of Cr^{+6} in various water resources, Various methods which has been adopted by the researchers for the effective removal of Cr^{+6} such as Membrane Separation, Bisorption, Ion-Exchange, Reverse osmosis, Adsorption etc. Various methods followed by the researchers using various raw materials to mitigate Industrial wastewater containing $Cr^{+}6$. Treatment of Cr^{+6} contaminated water by adsorption through resins has been discussed in details. Various applications of natural materials to prepare natural resins has been documented. Application of natural resins to reduce heavy metals has been reported.

Chapter 3 consists of Materials and methods that reports all the chemicals required for the preparation of Cassia 4-hydroxy benzoic acid resin, characterization of the resin using various analytical instruments, various instruments required to carry out the experimental procedure and preparation of stock solution for the study of batch experiments. It also deals with the explanation of adsorption isotherms and Kinetic models. Besides, it describes various proposed models to fit the column study data.

Chapter 4 deals with the results and discussions of the batch experiments being conducted. It reports various model parameters when fitted to various adsorption isotherms such as Freundlich, Langmuir, and Temkin etc. The kinetic experimental data were fitted to Pseudo-first order, Pseudo- second order, intra-particle diffusion, elovich model and has been analysed.

Chapter 5 deals with the adsorption of the Cr^{+6} from water by Cassia 4-hydroxy benzoic acid resin using statistical tool. Optimization of experimental parameters was achieved through Response Surface methodology by Box-Behnken design tool.

Chapter 6 consists of the results and discussions of the continuous fixed-bed column system and adsorption modelling including Thomas model, Yoon-Nelson Model and Adam –Bohart Model etc.

Chapter 7 provides conclusions relating to resin characterization, batch study, column study, as well as Box-Behnken Design.

Chapter 2

Literature Review

2.1 IMPORTANCE OF Cr^{+6}

Rapid development in population growth by the method of mining, extraction and use of several metals from industrial and domestic resources increases toxicity to a greater extent because of the production of various metal ions in the atmosphere. The areas around the metallurgical industries consist of wastes which deteriorates the environment. On the other hand some of these heavy metals, in traces, show a substantial part in the human metabolic rate. The demand of Cr^{+6} ought to be growing worldwide due to its widespread usage in several industries including metallurgy, leather tanning and chemical processing as they have different physical and chemical properties. Some of its essential uses are enumerated below:

- Cr^{+6} have a property of resistance to corrosion due to which it can be used to harden steel, stainless steel and alloys.
- The electro-plating industry uses Cr^{+6} as it provides a shining surface and used for hardening.
- Used in glasses for greenish tint.
- Used for Preparation of catalysts.
- Used as an oxidizing agent.
- Cr^{+6} being widely textile industry uses Cr^{+6} in the form of astringent.
- An aircraft industry uses Cr^{+6} to get rid of corrosion which could be used as an anodizing.
- Used in refractory industry to give a definite shape in the formation of aluminum bricks because of its high melting point, stable crystalline structure and moderate thermal expansion.
- Used as an agent for melting furnaces.
- Used in leather tanning industries.

Cr^{+3} play a major role in our body **[27]**. Absence of Cr^{+6} in our body fails to utilize protein content, sugar content and fat content that results in severe loss of weight and improper growth of the body, inadequate function of nervous system and diabetic situations. Contribution of Cr^{+6} is to regulate blood sugar with the help of insulin by way of radio tracing. When the glucose level of the body becomes high, the protein hormone known as insulin controls it by regulating blood inside the body.

Cr^{+6} are merchandized all over the world market in the forms of high quality ore with transitional ferrochrome because of its capability of handling different metallurgical commercial units. Different grades of ferrochrome have been utilized to get finished yields of modern skill. The use of other metals like co, Ni, V_2O_3, has been replaced with Cr^{+6} to make steels made up of alloys. Yet these are not known well because of their irrelevant advantages over Cr^{+6} like high cost. Thus, Cr^{+6} is said to be an essential element which is required to make refractory bricks and stainless steels by mixing metals in the alloy steels.

Deposits of Cr^{+6} in India can be found from Eastern Ghats **[28]** consisting group of rocks particularly in states of Andhra Pradesh and Tamilnadu. While deposits of iron ore known as (Dharwad) group can be obtained from states of Bihar, Orissa, Karnataka and Maharashtra. Few chromite deposits can also be found in Manipur, Nagaland and Assam.

Reports shows that Orissa consists about 98% of the total deposits of chromite in India mainly found in the belts of Sukinda valley near Jajpur district and belts of Baula-Nuasahi near Bhadrak district. Sukinda valley is situated at a zone covering 50 km in the east to west bordered by Mahagiri and Daitary ranges. There are total reserves of around 130 million tons of chromite zones found in India Chromite's are found under a depth of about 50-250 meters.

Present pollution scenario due to chromium in Orissa

Chromite reserves are found to be about 88.35 million tons in India from which about 35 million tons is recovered from metallurgical grades and about 78.4 million tons from mining activities. Low-quality ores is mostly used by chemical industry whereas high quality chromite is traced near the belts of Sukinda. The area under Sukinda is sharply worsened due to which there is a need for export of high-quality chromite and there is also a need of modification in the raw material so that ferrochrome or other chrome alloys are used to acquire value-added products. Due to the enhancement of price in raw materials and inadequate availability of chromite, domestic market utilizes high quality ores for the large scale production of chrome. The environment gets deteriorated by the discharge of Cr^{+6} effluents from mining industries. The details regarding discharge of the pollutants from various industries are given below:

A) Mining industries

The air consists of an enormous amount of dust which is discharged into the atmosphere through blasting, stacking, mining, loading and transport. Different surfaces for example area surrounding the forest canopy where the dust gets deposited can be drained out by rainfall. Here, chromite is mostly found in the form of dusts. The exposure to dust creates an influence on the respiratory channels of labors and occupants, which are received from the mines, cannot be controlled by the use of Water sprinkling technique. Water obtained from the mining operation is poisonous. Although Cr^{+6} occur in a trivalent state present in a chromite but biochemical conversions leads to the formation of some Cr^{+6} ions. Despite of insufficient treatment, the polluted water discharging from mines enters into the neighboring water resources. According to the measures taken by the Govt. regulatory bodies, chemical treatment methods was followed only by a few mining industries because of its higher cost involved.

B) Metallurgical industries

Dust: Due to the discharge of the dust into the atmosphere from handling of ore, reduction of arc, generation of power etc., immense measures are taken into account for the control of these dusts but the measures taken were not proved to be a satisfactory.

Slag: Cr^{+6} compounds are available in various valence states from the slag which has been disposed of over the ground. During the rainfall, Cr^{+6} saturates into the subsoil or physical water sources because of some chemical transformation. The obtained ferrochrome slags from the subsoil are allowed to get destroyed and drained out so as to recuperate the observing ferrochrome and the waste is disposed of in low lying terrains and pits. In this procedure some of the sludge is also produced which contaminates the water.

Water: Cooling water is allowed to blend with bichromate to use it in the process of cooling water towers for the prevention of the developed fungal growth or contagious Treatment of this water is essential to get rid of contaminated water which creates pollution.

C) Chemical industries (mainly bichromate manufactures)

Slag/Residue: Some of the sparingly soluble chromates and calcium carbonate are produced during the removal of chromates from the deposits. These soluble chromates being produced enters into the water bodies and form landfills slag which worsen the human health.

Dust: Dust unconfined after the process of roasting generates Cr^{+6} of higher concentration liberating dust to a larger extent that has a negative impact on the labors or workers health. Some traces of Cr^{+6} as a dust were also found in the nearby zones.

Water: Cr^{+6} is present in higher amount in the water bodies which leads to the contamination of various water resources.

D) Others

i) Leather tanning: Nowadays, leather industry is utilizing Cr^{+6} sulphates for tanning. During this process, Cr^{+6} extracted from chromates is almost found in its trivalent state so it cannot be defined as the main reason of concern. However, utilization of chromic acid or bichromate is required for the effective treatment of removal of Cr^{+6} from wastewater.

ii) Electroplating: Many electroplating industries have been developed due to which it's quite difficult to get adequate information. The wastewater contains high amounts of Cr^{+6} due to which labors are prone to airborne diseases.

A study has been conducted and it was observed that higher traces of chromium from the mines water resides in the sediments of river Brahmani and Dhamra at the meeting point of Bay of Bengal **[29]**.It is proved from the investigation that the wastes generated from metallurgical, chemical and refractory industries consists Cr^{+6} to a larger extent which is much higher as compared to the suggested limit for discharge. Cr^{+6} is found in higher amounts of about(0.252 to 2.8 mg/L) from open-pit areas and under-ground mining areas which was collected according to a survey done by RRL Bhuvneshwar in the year of 2000.The water discharged from the aquatic bodies is used by the villagers for public, national and irrigation purposes.

Plant and harvests life are greatly affected by the generation of Cr^{+6} from the mines and traces of Cr^{+6} is found mostly in their parts like roots, stems and fruits. Roughly roots of plants consists Cr^{+6} of about 60 mg/g, shoots of 14.5 mg/g Cr^{+6} and seeds of the plants consists about 2 mg/g which are the conditions required for growth of rice plant. Ferrochrome contains less Cr^{+6} comparatively to Cr^{+6} sulfate, Cr^{+6}dichromate and hence generates less pollution. Discharge of Cr^{+6} from these wastes deteriorates the atmosphere

2.2 TOXICITY OF Cr^{+6}

Trivalent Chromium (Cr^{+3}) and hexavalent chromium (Cr^{+6}) are the two forms of Cr^{+6} available in the earth's crust. Cr^{+6} essentially prove to be more contaminated than Cr^{+3}. The main organ which is affected by the toxicity of Cr^{+6} is known as respiratory tract and this organ is exposed to acute and chronic respiration problems. On severe exposure to Cr^{+6}, there was a rapid growth in the problem of respiration, coughing and wheezing but after the chronic exposure there were other respiratory effects, holes and ulcerations occurred and other disease like bronchitis and pneumonia increased. The study reports that intake of Cr^{+6} cause a bigger threat to lung cancer. In vitro and in vivo, mutation is caused by the intake of Cr^{+6} complexes for example, chromosomal abnormalities in an extensive variety of prokaryotic and eukaryotic so it was found that Cr^{+6} shows the mutagenic behavior **[30]**.

2.3 MUTAGENICITY

Reduction of mutagenic is done by decreasing gastrointestinal juice of humans. The differences in physical and chemical characteristics well describe the change in activities related to mutagenic on Cr^{+6} and Cr^{+3}.

2.4 CARCINOGENICITY

Taking into account the lung tumors, Cr^{+6} causes carcinogenicity which is observed in many studies of inhalation , In further studies, the Cr^{+6} was overseen by implantation or vaccination. Studies elaborates that cancer causing nature of calcium, lead, strontium, and zinc provides halfway confirmation for the cancer causing nature of Cr^{+6} trioxide along with sodium dichromate.

Table 2.1: Industrial wastewater containing Cr^{+6}

Industry	Cr^{+6} Conc (mg/ L)	References
Hardware factory	60.0	Xu *et al*. 2005 **[31]**
Chrome tanning plant	3.7	Gupta *et al*.1999 **[32]**
Electroplating plant	20.7-75.4	Kiptoo *et al*. 2004, Tukaram Bai *et al*. 2005 **[33,34]**
Tannery plant	8.3-3,950	Esmaeili *et al*. 2005, Song *et al*. 2000,**[35,36]**

Table 2.2: Permissible limits of Cr^{+6} in different water bodies

WATER RESOURCES	PERMISSIBLE LIMITS
River water	0.04–0.5 mg/litre
Ground water	(<1 mg/litre)
Drinking water	0.05 mg/litre

2.5 Cr^{+6} REGULATIONS

Cr^{+6} in the aquatic bodies have a great impact towards individuals, creatures, plants due to which few organizations employ strict regulatory measures .According to the World Health Organization (WHO) consumption has set an permissible limit of 0.05 ppm for Cr^{+6} removal and 2 mg/L of about 2 mg/L in drinking water [14]. The Maximum Contaminant Level (MCL) is found to be 0.1 mg/L from total Cr^{+6} content according to the survey by world health organization. Cr^{+6} less than 50 ppm observed some fluctuations in the colour change. Cr^{+6} can be reused further as a part of feedstuff for creatures. It was found to have Cr^{+6} at levels below 2.75% of the whole by weight. The permissible limit for health hazards and safety has been stated as 15 mg/m3 by National Institute for Occupational Safety and Health (NIOSH) and 0.001 mg/m3 as stated by Suggested Exposure Limit **[37]**.

2.6 METHODS TO REMOVE Cr^{+6}

2.6.1 MEMBRANE SEPARATION

A.E. Pagana *et al* [38] work was based on the removal of arsenic and Cr^{+6} ions from polluted water using porous membranes of ceramic, membranes of composite c-al2o3 by the process of sol-gel method. The process separates the combined adsorption-ultrafiltration process **Moura *et al* [39]**considered the Cr^{+6} evacuation by a membrane separation technology where ions gets transferred from one phase to the other by the driving force applied with the help of an electric field. The process of electro dialysis was followed by the author by mixture of polymers known as polystyrene and polyaniline for the production of membrane. Hence the desired membranes produced can be utilized for the removal of metal ions from tannery as well as metal finishing industries. **Christina –Veronica Gherasim *et al* [40**] dealt with a polymer inclusion membrane (PIM) as an adsorbent which is prepared by liquefying a polymer, a separating agent, and a plasticizer mixed all together in a suitable dissolving solvent and then, afterwards this dissolvable solvent was allowed to evaporate at absolute room temperature. This developed thin and stable films membrane was further used for Cr^{+6} removal The studies also shows the different effects on variation of contact time, pH as well as Cr^{+6} concentration by batch process. **MA. Hassan *et al* [41]** used liquid emulsion membrane (LEM) for further analysis of the research for recovery of Cr^{+6} . The Tri- octylphosphine oxide (TOPO) which has been used as a carrier, cyclohexane as an natural diluent, sodium hydroxide for stripping of a solution with Span-80 (sorbitain monooleate) to emulsify the solution were used for the preparation of this liquid membranes.

2.6.2 ADSORPTION

Cr^{+6} can be removed from waste water through the process of adsorption. Some of the natural adsorbents like bentonite, agricultural residues, oil cakes, activated charcoal, and activated carbons are used to study the adsorption process. **Mbaye Gueye *et al* [42**] researched on the adsorption process developed by activated carbons (AC) using Jatropha wood and peanut shells. Effect of pH and acid/base nature on the surface of activated carbon is also considered to have an idea about the mechanism process of adsorption which is due to the phenomena of electrostatic attraction **Mani Arulkumar *et al* [43]** used prawn shell activated carbon (PSAC) for the Cr^{+6} removal by Response surface methodology (RSM) for the optimization of various optimum conditions The isotherms including Freundlich and Langmuir both fits well and the kinetic studies proves that it follows a pseudo second order reaction. **Hong Zhang *et al* [44]** studied Cr^{+6} removal by using activated carbon derived from the residues of algal bloom. Various effects of process variables such as amount of adsorbent, pH of the solution; initial Cr^{+6} concentrations were also used for the effective removal of Cr^{+6}. At pH 1, there occurs a favorable adsorption. The adsorbent was characterized using scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR) to study the mechanism related to the process of adsorption.

Z.A. AL-othman *et al* [45] studied the process of adsorption on Cr^{+6} using activated carbon being prepared from the peanut shell. The characterization of carbons prepared was done by BET analyzer for the calculation of surface area and pore size distribution The factors including pH, contact time, initial concentration, temperature has also an impact of on Cr^{+6} adsorption were also investigated.

2.6.3 BIOSORPTION

Ihsan Ullah *et al* [46] studied the adsorption of Cr^{+6} by utilizing the sugarcane bagasse prepared from biomass residues. The Immobilized sugarcane obtained from the biomasses residues were taken as a function of initial Cr^{+6} concentration, amount of adsorbent, pH and contact time for the effective Cr^{+6} removal from the tannery industries were also investigated..

Sharma Mona *et al* [47] worked on the biosorption of Cr^{+6} using RSM Method by utilizing cyano-bacteria which is an waste derived from the biomass residues of Nostoc linckia .The adsorbent obtained was in the form of alginate beads which was further used for the analysis of various optimum parameters. **Ahmet Sari [48]** studied the adsorption potential for Cr^{+6} removal using red colored algae rock which is also known as Ceramium virgatum. The advantage of using these algae as an adsorbent is because of its renewable, naturally available and hence it is proved to be cost-effective. The effect of various process variables like pH, contact time, amount of adsorbent and temperature were studied. The Langmuir model fits well to this adsorption process among all models being applied. **Ozgur Dogan Uluozlu *et al* [49]** confirmed adsorption conditions as a function of variation in pH, amount of biomass, temperature and contact time on basis of research related to the adsorption on Pb^{2+} and Cr^{3+} ions from water solutions by using the lichen (Parmelina tiliaceae) derived from the biomass. **XU Han *et al* [50]** studied Cr^{+6} removal using Chlorella miniata. The factors on which the equilibrium time depends are initial pH, biomass dose and Cr^{+6} concentrations and the maximum removal can be attained at initial pH of 3.0 from the reported equilibrium data's.

Durali Mendil *et al* [51] reported Cd^{2+} and Cr^{3+} ions removal by the use of moss (Hylocomium splendens) biomass. Since 20 years, mosses have been used as bio monitors to determine the heavy atmospheric metal deposition due to its higher cation exchange capacity.

2.6.4 ION-EXCHANGE

Beharang Pakzadesh *et al* [52] evaluated the removal of Cr^{+6} using synthetic ion-exchange brines and calcium polysulfide for determining the effects of Cr^{6+} concentration, calcium polysulfide dosage, pH, and ionic strength in process of adsorption. **Petruzelli *et al* [53]** reported process known as the IERECHROM process which is based on the concept of using macro-porous carboxylic resin that helps in the Cr^{+6} removals. **Chmielewski *et al* [54]** discovered a method by using a process of electrochemical oxidation and ion exchange for the removal of Cu and Cr^{+6} from the water originating from electroplating industries. **Lin and Kiang [55]** developed a procedure using multi step ion exchange process through regeneration of the chemicals used to remove the chromic acid from a contaminated waste water stream. **Yalçin *et al* [56]** studied Dowex 50X8, a strongly acidic cation-exchange resin, to recover the two forms of Cr^{+6}using the process of oxidation and reduction from the wastewater originating from electroplating industries. **Rengaraj *et al* [57]** used three sets of ion exchange resins namely as 1200H, 1500H and IRN97H in the pH ranging from 2-6 and initial chromium concentration of 10mg/l for Cr^{+6} removal. The adsorption process follows both Langmuir as well as Freundlich isotherms. It also obeys Pseudo second order kinetics. **Sofia A. Cavaco *et al* [58]** studied the removal of Cr^{+3} by using a chelating exchange resin (Diaion CR11) and a weak cationic resin (Amberlite IRC 86) at two different temperatures respectively while other parameters including , pH, time and concentration were kept as constant to determine the capacity of the resins.

Gulten Cetin *et al* [59], conducted research on removal of Cr^{+3} by using the resin Amberjet 1200Na having a matrix of styrene-divinylbenzene by using the process of multisorption and regeneration cycles of the resins by using hydrogen peroxide in alkali media and kinetics of the oxidative regeneration were also performed. **F Gode *et al* [60],** studied the Cr^{+3} removal by using a pair of resins such as chelating resins Chelex-100 (from Merck) and Lewatit TP 207 (from Bayer) .The maximum adsorption capacity for Cr^{+3} ions was observed at pH 4.5. Both the resins are proved to have good binding capacity because of the presence of functional groups like styrene- divinylbenzene matrix and iminodiacetic acid groups in a styrene matrix present in it.

RESINS

Resins are used to purify contaminated water such as synthetic and natural resins**. Harbi *et al* [61]**; used Dowex 1X8 resin for effective Cr^{+6}removal by Batch process. Several optimum parameters like resin dosage, contact time and temperature were considered during the batch study operations .The process of adsorption was followed by Freundlich isotherm and obeys the pseudo second order model. **L.Rafati *et al* [62]**; used Lewatit FO36 ion-exchange resin for the efficient removal of Cr^{+6} ions by varying the different conditions as variation in amount of resin, initial Cr^{+6} concentration, contact time and pH. The Kinetic studies in this process follows Pseudo second order model. .**S.Bajpai *et al* [63]**; studied Amberlite SR1L Na resin for the removal of Cr^{+3} ions by varying the pH from (2-5), resin dose as (5-25 g/L), initial Cr^{+3} concentration as (50-300 mg/L) and contact time as (0- 150 min.) .**M.A Barakat *et al* [64]**; studied the effect of removal on Strong anion exchange resin known as Spectra/Gel IE 1x8 .Various process parameters including pH, Cr^{+6} concentration and amount of resin and adsorbent concentration and contact time are also considered based on the conducted experiments. Maximum adsorption capacity of the Cr^{+6} reached up to 173.8 mg/g. The isotherms model fits well to the Langmuir models. **S. Rengaraj *et al* [65];** observed that the resins 1200H, 1500H and IRN97H demonstrates a significant growth in adsorption capacity of Cr^{+6}, related to former .It fits well to Langmuir as well as Freundlich isotherms and follows first-order reversible kinetics and pseudo-second-order kinetics. Ibrahim et all; used a synthetic resin known as Amberlite IRA 400(Cl) resin and obtained a highest % adsorption of 99.92 % at 30 ppm of Cr^{+6} concentration. **N. Kabay *et al* [66]**; studied the process of adsorption using impregnated resins known as Aliquat 336 to remove Cr^{+6} from the wastewater system. The process gets well fitted to Langmuir isotherm. **Catalin Balan *et al* [67];** has used anionic resins known as, purolite A-400 along with purolite A-850 made up of gel like structure. The maximum percentage of Cr^{+6} removed observed was 99% at pH varying from 4.0–5.3 with amount of resin as 6 g/L and initial concentration of 100 mg/L. The resins consists maximum adsorption capacity as 120.55 and 95.82 mg respectively and it also stated the adsorption process follows pseudo second order model. Some of the natural materials are being used over synthetic resins due to the fact of high price in petrochemical products. Few natural materials such as guar powder, tamarind kernel powder, Xanthium gum powder, Sesbania gum powder etc. has been employed into account by various researchers for the effective removal of metal ions. The resins prepared from these natural materials have an advantage over synthetic resins like these are non –biodegradable and cost-effective. **Archana Chahar *et al* [68];** prepared tamarind 8-hydroxyquinoline-5-sulfonic acid resin and studied the characterization of the resin by FTIR (Fourier transform Infrared) spectra ,total ion exchange capacity and elemental analysis .The effects of various different conditions like pH, treatment time, temperature, resin quantity with variation in the rate of flow are maintained to remove Cr^{+6} from the industrial discharges **A.V Singh *et al* [69];** used a guar gum-based resin which consists of nitrilotriacetic group .The characterization of the (GNTAA) resin was done by using FTIR, BET analyzer, ion exchange capacity, thermogravimetric analysis as well as CHNS analysis. This research also emphasized on various factors which has a great impact on pH, distribution coefficients (K_d) to study the % removal of Cr^{+6}. **Q. Zhang *et al* [70];** used Sesbania gum supported dithiocarbonate chelating resin(SGDSA)for the effective removal of Cr^{+6} ions based on the reaction of epoxidation. Subsequently, Cassia gum powder, a natural material acquired from seeds of endosperms of Cassia tora and cassia obtusifolia which belongs to leguminosae family has been utilized to prepare natural resin. This tree is mostly grown in tropical region and has high therapeutic properties.

2.7 OBJECTIVES

The main objective of our research is to remove Cr^{+6} from water using natural resin.

The specific objectives are:

- Preparation and characterization of natural resin.
- Optimization of process condition to remove Cr^{+6} using batch studies.
- Optimization of batch experiment using statistical tool.
- Continuous removal of Cr^{+6} from contaminated water using column study

Chapter 3

MATERIALS AND METHODS

3.1 PREPARATION OF ADSORBENT

3.1.1 PREPARATION OF RESIN

Preparation of Resin from cassia gum powder involved two steps: initially epoxy propyl ether of cassia was prepared followed by reaction with 4-hydroxybenzoic acid to produce cassia 4-hydroxy benzoic acid (CHBA) resin. The detailed process for preparation of the resin is depicted through Schematic layout as per figure 3. 1and figure 3. 2. A definite quantity of cassia gum powder was slurred with dioxane in a round bottom flask. Subsequently 0.1N NaOH solution was added to make it alkaline. The contents were stirred continuously with addition of epoxychloropropane at 60^0 C for 5 hours. The obtained product called epoxy propyl ether of cassia hence parted from the above solution when centrifuged on 3000 rpm aimed at 15 minutes. Impurities in the obtained product were further removed by washing with methanol and were further dried with the help of hot air oven at 40 ^{0}C. During the next step the obtained epoxypropyl ether of cassia was reacted with 4-hydroxybenzoic acid while constant stirring at 60^0 C for 5 hours and was left overnight to settle. Further separation of resin was achieved by centrifuging at 3000 rpm and subsequent washing with 90 % methanol with few drops of HCl to obtain a pure resin named as Cassia 4-hydroxybenzoic acid resin. The CHBA resin produced was acid washed with dilute HCl (0.1N) to create hydrogen group on the surface. The double distilled water is used to wash the CHBA resin so that the excessive acid present in the resin gets removed and the sample was dried at 313 ^{0}K in oven and stored in a steel container till further used.

Step 1.Preparation of epoxypropyl ether of Cassia

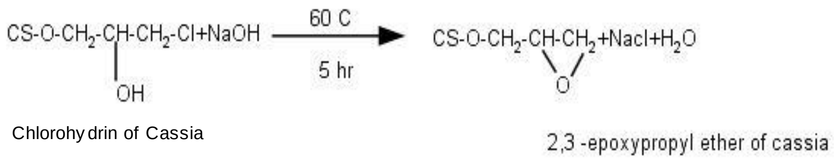


Figure 3.1: Preparation of epoxypropyl ether of cassia

Step 2: Preparation of Cassia 4-hydroxybenzoic acid(CHBA)resin

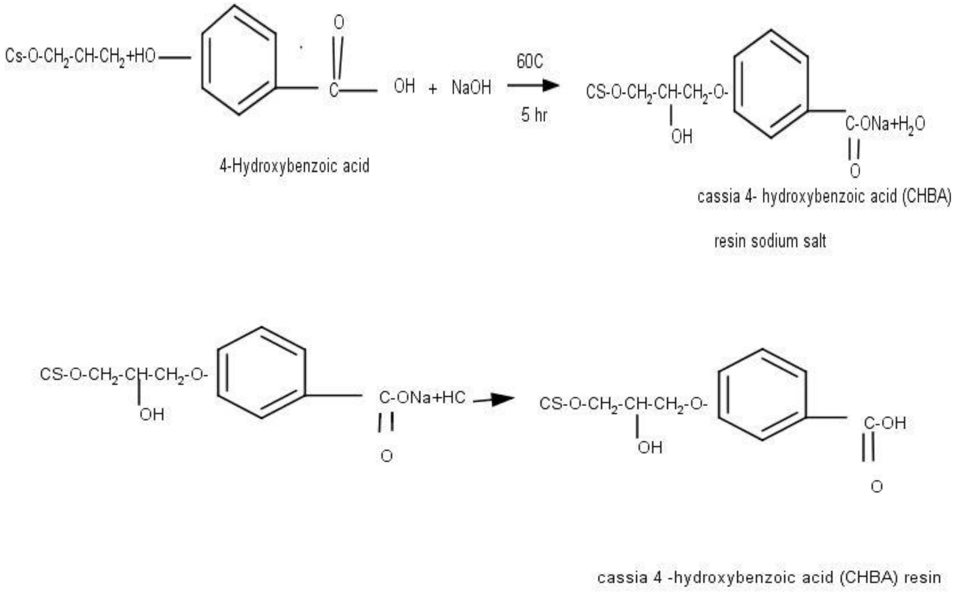


Figure 3.2: Preparation of Cassia 4-hydroxybenzoic acid (CHBA) resin

3.2 CHARACTERIZATION OF ADSORBENT

3.2.1 FTIR ANALYSIS

The FTIR analysis was used to determine the various functional groups present in the resin sample. The FTIR analysis was done with the help of FTIR-3500 spectrophotometer. The resin was crushed by 200 mg of KBr (spectroscopic grade) which is placed in a mortar and compelled into 10 mm which was then used to detect the functional group analysis.

3.2.2 CHNS ANALYSIS

An elemental analyzer purpose is to offers a pathway for finding the carbon, hydrogen, nitrogen and Sulphur contents or percentage in the resin.

3.2.3 NITROGEN CONTENT

The Kjeldahl's method is the ordinary method to find the nitrogen content, the dried resin consisting weight of 0.2 g was taken inside a dried Kjeldahl's flask and concentrated sulphuric acid of 10 ml was mixed in the flask with 0.60 g of catalyst was also added into the flask and the above solution was allowed to heat for 2 hours. After heating, the mixture of solution was allowed to cool and then it was transferred to a distillation unit along with 20 ml of distilled water to determine the ammonia. Subsequently, volume of 12 ml consisting 10 N of sodium hydroxide was allowed to mix and to make up total volume residing in the flask to 75 ml. The ammonia was then liberated which was steam distilled continuously for 5 minutes containing 5 ml of 4% boric acid and 5-6 drops Phenolphthalein indicator. The ammonia which was distilled was further titrated with the help of 0.05 N hydrochloric acid.

3.2.4 TOTAL ION EXCHANGE CAPACITY

Titration procedure was done in which resin weighing 1 g was allowed to convert into its hydrogen ion form; and the wet resin consisting of 1 g was taken in an Erlenmeyer flask with 200 ml of sodium hydroxide solution of 0.1000M, 25 ml of the above supernatant liquid was taken for further titration by using standard solution of 0.05 N HCl with the help of phenolphthalein indicator. The resin which was left in H+ forms was used for calculating the moisture content in the resin. Capacity of the resin is calculated brlow mentioned formulae.

$$\textbf{Capacity of the resin} = \frac{mL_{NaoH} \times M_{NaoH}}{mass_{resin}} \qquad \ldots 3.2.1$$

Where mL_{NaOH} - Volume of NaOH used to titrate.

M_{NaOH} - Normality of NaOH.

Mass $_{resin}$ - Mass of resin used (grams, air dried).

3.2.5 MOISTURE CONTENT

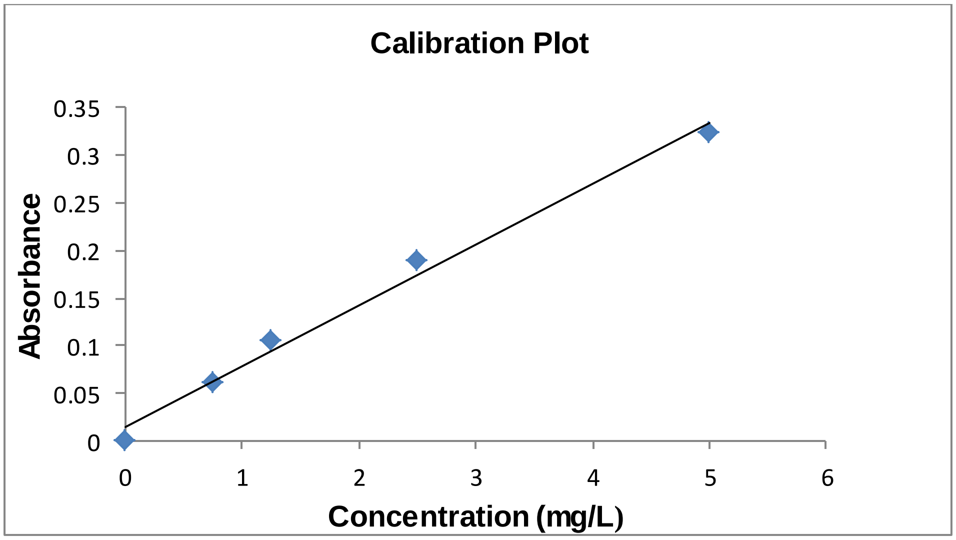
Firstly the resin in its hydrogen form of a specified amount of 1 g is weighed accurately and placed into a predried, cooled and tared moisture dish. The dish is then placed in an oven operating at a specified temperature of 110^{o}c maintained for 1 hour then the resin was taken from the oven and allowed to cool in a room temperature for 15 minutes. The resin was then allowed to dried to a constant weight in a vaccum dessicator at 30ºc for 24 hours and then the resin was weighed.

3.3 CHEMICALS

All chemicals used in the experiment were Analytical grade namely Epichlorohydrin (Sisco Research Laboratories, Mumbai), 4-hydroxy Benzoic Acid (loba chemie Private Limited), sodium hydroxide, Methanol and HCl (Sigma Aldrich, Mumbai), Dioxane (sico research laboratories, Mumbai), potassium dichromate (Merck, India) were processed for synthesis of resin. Cassia gum Powder was procured from Bhairav industries, Ahmedabad, India.

3.4 STOCK SOLUTION PREPARATION

Standard Cr^{+6} solutions of different concentrations ranging from 0.5 to 5 ppm have been prepared. Absorbance have been measured for all the prepared solutions at 540 nm using UV-Vis Spectrophotometer. The instrument was calibrated using distilled water as reference before starting of the experiment. A calibration curve was prepared between concentration of Cr^{+6} solutions (mg/L or ppm) vs corresponding absorbance (nm) as shown in Figure- 3.3.



. **Figure 3.3: Calibration plot for Cr^{+6}**

3.5 METHODOLOGY

Various equipment's are used in preparation of resins such as pH meter (Systronics, 361) to maintain the pH of the solution, centrifuge (cooling Eppendorf centrifuge, 5702 RH) to separate the resins from solution, constant temperature magnetic stirrer (Remi, 2MLH),) to maintain the temperature while constantly stirring the ingredients during resin synthesis; hot air oven (Ricco, India) for drying the prepared resin. Surface Characterization of resin was essential to understand the properties of the developed resin. FTIR studies were performed to know the surface functional groups using Nicolet TM 10, Thermofisher scientific, and USA. Amount of Cr^{+6} adsorbed by the resin was estimated using UV-Vis Spectrophotometer at 540µm wavelength (UV-3200 Double Beam Spectrophotometer, Lab India) using 1,5-diphenylcarbazide method **[71]**

FTIR: The instrument namely as Fourier transform infrared spectroscopy instrument is used to determine the functional groups present in a metal ion with the help of KBr pellets. The resin has to be converted to its H+ form firstly before carrying out the FTIR analysis.

CHNS: An elemental analyzer purpose is to offers a pathway for finding the carbon, hydrogen, nitrogen and sulphur contents or percentage present in the resin.

PH meter: It was used to measure the pH (acidity or alkalinity) of the sample consisting Cr^{+6} with resin. The pH of the samples should be around 6-7.

Constant Temperature Shaker: It has been used for the experimental batch study.

UV-Vis Spectrophotometer: It has been used for the measurement of Cr^{+6} concentrations.

Centrifuge: It was used to separate the mixture of two distinct densities which was also further being used for separation of resin.

Magnetic Stirrer: It is used for the preparation of resin.

3.6 ADORPTION MECHANISMS

Adsorption experiments under varying optimum parameters like pH, amount of resin, contact time, amount of Cr^{+6} concentration is carried out by adding required amount of resin consisting in 250 ml flasks each comprising 100 ml Cr^{+6} solution. pH was varied from 3-11 with the help of 0.1 N HCl in addition to 0.1 N NaoH solution. The contents inside the flask were shaken inside an incubator shaker (Reico, India) at a definite shaking speed (130rpm) and temperature 30^0 C. After adsorption, the residual Cr^{+6} concentrations were estimated by the means of UV-Vis spectrophotometer and the corresponding wavelength should be 540 nm. The influence towards adsorbent dosage on percentage removal efficiency for the studied resin was achieved through changing the resin amount starting from 0.1 g to 1 g for a definite Cr^{+6} concentration with observing other optimum parameters (pH, shaking speed, contact time as well as temperature)constant according to the optimum values obtained from previous experimentation. Percentage removal of the resin was obtained using the following expression as given below:

$$\textbf{Percentage Removal} = \frac{C_{o}-C_{e}}{C_{o}} \qquad \textbf{… 3.6.1}$$

Where C_o and C_e (mg/L) are the initial and outlet concentration of metal ions in solution.

3.7 ADSORPTION ISOTHERMS

A correlation among adsorbate amount adsorbed on a resin surface at a definite temperature and the equilibrium concentration of adsorbate achieved after contact with adsorbent is termed as adsorption isotherm. Experimental data can be verified through diverse adsorption isotherm models like Langmuir, Temkin, Dubinin Radushkevich and Freundlich.

3.7.1 FREUNDLICH ISOTHERM

Freundlich equation is used to derive the model onto a multilayer surface of adsorption and adsorption taking place on heterogeneous surfaces. It is established with the assumption that each component has one exponential distribution of energy related to adsorption. The equation of Freundlich model is specified by (Freundlich and Heller, 1939). The logarithmic form of equation

$$log\frac{x}{m} = logK_F + \frac{1}{n}logC_e \qquad \textbf{… 3.7.1}$$

Where x relates to quantity of Cr^{+6} being adsorbed (mg),m known as mass of the adsorbent in grams, C_e relates to equilibrium concentration in (mg L^{-1}), K_F , 1/n exist as the constants of Freundlich equation,1/n known as factor of heterogeneity in addition to k_F that indicates the capacity of adsorption. The values with n>1 reflects the favorable adsorption. The slopes, intercepts are found from the linear plots consisting log(x/m) versus log c_e for different adsorbent doses and also the data of n and k_F can be calculated with the help of these slopes, intercepts **[72].**

3.7.2 LANGMUIR ISOTHERMS

This model equation was first established by Langmuir in 1948. It was constructed on the postulation that homogeneous surfaces are required for adsorption to take place and it occurs due to monolayer coverage. The equation of Langmuir isotherm can be represented by:

$$\frac{C_e}{q_e} = \frac{C_e}{C_m} + \frac{1}{K_L C_m} \qquad \textbf{… 3.7.2 (a)}$$

Where C_e represents the equilibrium concentration of the Cr^{+6} solution in (mg L^{-1}) and q_e (mg g^{-1}) equilibrium capacity of adsorption. The C_m indicates the capacity of adsorption in (mg g^{-1}) when a complete monolayer surface is achieved and k_L is linked with affinity towards binding sites. The intercept, slopes were found using the plots (C_e/ q_e versus C_e) which were then correlated to find values of k_L and C_m. The viability and favorability of the adsorption process can be stated by a constant known as separation factor (R_L) which is almost dimensionless. The dimensionless data's (R_L) was calculated with the help of equation as followed:

$$\boldsymbol{R_L = \frac{1}{(1+K_L C_o)}} \quad \textbf{… 3.7.2(b)}$$

Where C_o represents initial Cr^{+6} concentrations in (mg L^{-1}). The R_L should lie between 0 and 1 to get an adequate adsorption, whereas R_L>1 signify inadequate adsorption, and R_L=1 denotes rectilinear adsorption however the process becomes irreversible when R_L=0 **[73].**

3.7.3 TEMKIN ISOTHERM

Temkin isotherm takes into account an element that describes the relations amongst adsorbing rectilinear and the process of adsorption which is described by a constant dissemination of energies binding to each other. The equation describing Temkin isotherm is stated as:

$$\boldsymbol{q_e = B_1 \ln K_T + B_1 \ln C_e} \quad \textbf{… 3.7.3}$$

Where q_e relates to the quantity of metal ion which gets adsorbed per definite of adsorbent amount in (mg/g), C_e denotes as concentration at equilibrium is (mg/L), K_T is constant of binding metal ions at equilibrium condition in (g_{-1}) and the values of K_T and B1 can be found by plotting a linear graph between q_e and ln $C_{e.}$

3.7.4 DUBININ–RADUSHKEVICH ISOTHERM

. The D-R equation can be stated as below:

$$\boldsymbol{\ln q_e = \ln q_s - B \in^2} \quad \textbf{... 3.7.4}$$

Where B is defined as a constant of adsorption of residing energy, R (8.314 $Jmol^{-1}$ K^{-1}) denotes gas constant, and T (K) defines as total temperature and ε = RT ln (1 + 1/Ce). The constant B (mol^2 KJ^{-2}) tells the adsorption involving mean free energy of each and every molecule of the adsorbate as soon as the energy is transported to the outer layer of the solid .The factor which is used here provides data related to determine whether the adsorption process is chemical or physical .If the values of E is within the range of 8 and 16 KJ mol^{-1}, then, the process of adsorption is said to be a chemical ion-exchange, whereas if E< 8KJmol^{-1}, then the process of adsorption is followed by a physical nature**.[74]**

3.8 ADSORPTION KINETIC STUDIES

At a fixed optimum condition, the contact time was taken by means of a function when the resin was allowed to get adsorbed on the Cr^{6+}surface .Different Tests were conducted using definite amount of resin at varying initial concentration of Cr^{6+} to verify the order followed by the process of adsorption using Pseudo-first order kinetics, Adsorption kinetics using Pseudo-second order, diffusion study of Intra-particle, elovich model **[75].**

3.8.1 PSEUDO-FIRST ORDER MODEL

The capacity of adsorption of the solid system was fully dependent on the first order Pseudo kinetics or Lagrengen rate equation of the kinetics involving adsorption of liquid system to the solid system .This model has an important feature for determination of the adsorption rate equations originating from solution as a liquid form. The equation of Langrangen model is represented as (Ho and McKay, 1999a):

$$\frac{dq_t}{dt} = K_f(q_e - q_t) \qquad \textbf{...3.8.1(a)}$$

Where k_f (min^{-1}) denotes the constant adsorption rate of first order Pseudo-Kinetics, q_t (mg/g) is described as the capacity of adsorption during the time interval of t (min) while q_e in (mg/g) is said to be the adsorption capacity when the process is in its equilibrium state. Integrating the above equation by applying the conditions as: when t=0, qt =0 while when time reaches an interval of t min, that is t = t, then q_t becomes q_t=q_t.: the above equation can be written as:

$$\textbf{Log } (q_e - q_t) = log q_e - \frac{K_f}{2.303} t \qquad \textbf{...3.8.1(b)}$$

The plots between log (qe −qt) and t gives the value of the constant rate of adsorption that is, $k_{f.}$

3.8.2 PSEUDO-SECOND ORDER MODEL

The equation of second order Pseudo model is expressed elsewhere (McKay and Ho, 1999).

$$\frac{dq_t}{dt} = K_s(q_s - q_t)^2 \qquad \textbf{...3.8.2(a)}$$

Where the rate of constant that is, k_s will be in (g/(mg min) ,The slopes and intercept of the plots provides the values of constants k_s ,qe. Further integrating the above equation at the following conditions:

When t=0, qt =0 while if time reaches the interval of t min then, qt = qt .

$$\frac{t}{q_t} = \frac{1}{K_s q_e{}^2} + \frac{1}{q_e} t \qquad \text{...3.8.2(b)}$$

The plots between t/q_t and t provide the values of q_e when the process will be in its equilibrium state.

3.8.3 INTRAPARTICLE DIFFUSION STUDY

As per the Postulation of this study, the uptake capacity varies proportionally with $t^{1/2,}$ and weber-Morris plot (q_t versus $t^{1/2}$).

$$q_t = K_{id}\sqrt{t} + C \qquad \text{…3.8.3(a)}$$

Where k_{id} can be defined as the constant rate of intra-particle diffusion. The intercept (c) data describes the boundary layer thickness.

3.8.4 ELOVICH MODEL

The process of activated chemisorption can be only found by elovich equation.

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \qquad \text{…3.8.4(b)}$$

Where, the constants are known as a, b. The rate of initial adsorption in (mg/(g min)) is given by the a, and The energy required for activation of sites is given by the constant b which is used in chemisorption in (g mg^{-1}) while q_t in (mg g^{-1}) can be described as the quantity of Cr^{+6} required for adsorption during the time interval of t min. The plots between q_t and ln t gives the corresponding a and b values.

3.9 THERMODYNAMIC FACTORS

The information related to data's were derived from the isotherms of adsorption at different resin dosages and also variation in the temperature was also required for the calculation of parameters of thermodynamics like Gibbs free energy ΔG change, change of enthalpy ΔH as well as change of entropy ΔS. The constants K_L from the Langmuir equation, is required for calculating Gibbs free energy change as per the equations:

$$\Delta G = -RT \ln K_L \quad \text{… 3.9(a)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{…3.9(b)}$$

From equation (13) and (14)

$$\ln K_L = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{…3.9(c)}$$

To estimate the change in enthalpy and entropy a plot between ln K_L and 1/T was used**. [75]**

3.10 FIXED BED ADSORPTION STUDIES

Cassia gum powder based resins (CHBA) prepared were packed in a column made of perplex sheet. A representation of the experimental arrangement used to study the continuous flow in a packed bed column is shown in Figure.3.4. The internal thickness of the column tube and column height was taken of 1.2 cm and 10 cm correspondingly. The bottom part of the column was filled with cotton wool on the sieves attached to the column. The D_2O water must be evenly distributed to column containing the resin so that the impurities from the resins could be removed.

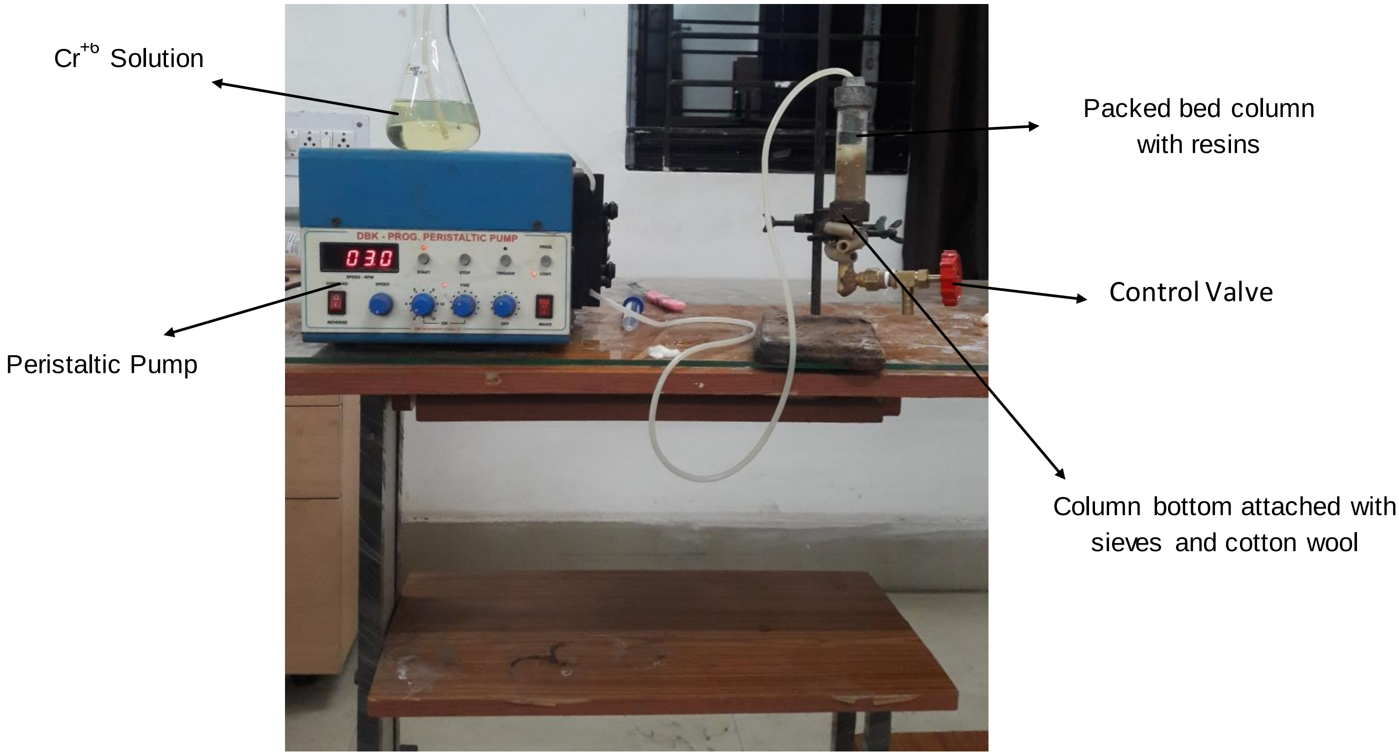


Figure 3.4 Packed Bed experimental setup

3.11 ANALYSIS OF COLUMN DATA

The Cr^{+6} solutions to be treated were permitted to flow under gravity inside the column. This respective flow was controlled and monitored using peristaltic pump [DBK-PROG PERISTALTIC PUMP]. The inlet and outlet ends of the column were controlled by using two valves. Influence of bed height, rate of flow and Cr^{+6} initial concentrations were studied by packing the column with CHBA resin up to 6 cm height (approximately 6.3 grams). At 20 ppm initial Cr^{+6} concentration, the flow rates were varied as 3, 5 and 7 ml/min to conduct the required experiments. similarly to investigate the change occurring in bed height, at a fixed rate of flow(3 ml/min) and Cr^{+6} initial concentration (20 ppm), the height of the bed column was changed from 2 cm (2.1 g), 4 cm (4.2 g) and 6 cm (6.3 g). From these above studies flow rate and height were fixed at optimum condition and Cr^{+6} initial concentration was varied from 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L. In each experiment, a fixed volume of treated Cr^{+6} solution was collected from the bottom after every 1 minute interval and solution concentration existing could be estimated using Varian UV Spectrophotometer.

Effective volume can be obtained from the equation 3.11(a) below:

$$\boldsymbol{V_{eff} = Qt_{total}} \qquad \textbf{...3.11(a)}$$

V_{eff} relates to collection of the effective volume in (ml); Q denotes as volumetric rate of flow in (ml/min): t_{total} represents total time taken to flow in (min).

The maximum bed capacity can be found by the equation by keeping the rate of flow and concentration fixed as:

$$\boldsymbol{q_{total} = \frac{Q\int C_{ad}dt}{1000}} \qquad \textbf{...3.11(b)}$$

q_{total} represents maximum capacity of bed in (mg); Q defines the rate of flow inside the bed in(ml/min); C_{ad} is the Cr^{+6} concentrations which is adsorbed in (mg/L). Using the plot between adsorbed Cr^{+6} concentrations verses time, the area under the curve can be calculated which gives the value of integral in equation 3.11(b).

The net volume of Cr^{+6} introduced to the column bed is represented as in equation: 3.11(c)

$$\boldsymbol{M_{total} = \frac{C_0Qt_{total}}{1000}} \qquad \textbf{...3.11(c)}$$

Where M_{total} is total quantity required of Cr^{+6} to feed inside the bed column (g); C_0 initial Cr^{+6} concentrations in (ppm); t_{total} denotes total time required to flow in (min).

Thus using equation 3.11(d) below we obtain the total percentage of Cr^{+6} ion removed.

$$\%\,\boldsymbol{removal} = \frac{\boldsymbol{q_{total}}}{\boldsymbol{M_{total}}} \times \mathbf{100} \qquad \textbf{...3.11(d)}$$

q_{total} total adsorbed quantity of Cr^{+6} (mg) ; M_{total} is total quantity of Cr^{+6} introduced to the bed of the column in (g).

Equilibrium The uptake capacity of Cr^{+6} at equilibrium is represented as 3.11(e):

$$\boldsymbol{q_{eq(exp)}} = \frac{\boldsymbol{q_{total}}}{\boldsymbol{x}} \qquad \textbf{...3.11(e)}$$

q_{eq} (exp) is rate of uptake capacity of Cr^{+6} in equilibrium (mg/g) ; q_{total} denotes maximum adsorption capacity of bed in(mg); X is quantity of resin required for column study in (g) **[76].**

3.12 MODELING OF FIXED BED COLUMN STUDIES ON RESINS (CHBA)

The Designing of full scale column operation use of data from laboratory based experiments is essential. The breakthrough curve and concentration profiles are essential features which are required for the column study and capacity of the adsorbed resin under some fixed operating condition is also required to effectively design the column. Besides this, the maximum capacity of adsorption in column is also equally important to be estimated for some of the adsorption systems. Numerous mathematical models were proposed to evaluate the effectiveness and feasibility of the models of column which are required for large scale industrial operations. Dynamic behavior of adsorbent adsorbate system can be studied using Thomas model, Adam –Bohart model as well as Yoon-Nelson model.

3.12.1 THOMAS MODEL

Thomas model is widely used solutions in column performance studies which assume the behavior of Plug flow in the Column bed. The process of adsorption in this model is limited as well as the external and inner diffusion are also absent. The following expression represents Thomas model for adsorption studies:

$$\boldsymbol{q}_{\boldsymbol{e}=\frac{\boldsymbol{RT}}{\boldsymbol{b_f}}\ln(\boldsymbol{k_f C_e})} \qquad \textbf{...3.12.1(a)}$$

Linear Equation of Thomas model is stated as

$$\ln\left[\left(\frac{\boldsymbol{C_0}}{\boldsymbol{C_t}}\right) - \mathbf{1}\right] = [(\boldsymbol{k_{Th} q_0 x/Q}) - \boldsymbol{k_{Th} C_0 t}] \qquad \textbf{...3.12.1(b)}$$

k_{Th} in (ml/min.mg) is defined as rate of constant of Thomas model; q_0 (mg/g) is adsorption capacity of Cr^{+6} at equilibrium condition for each gram of quantity of resin; q_e (mg/g) is sorption capacity; C_0 in (mg/L) is concentration of chromium at the inlet end; C_t in (mg/L) is concentration of chromium at the outlet end during the time interval of t min. C_t/C_0 represents relationship between Cr^{+6} concentration at the outlet end to the inner end. At a fixed flow rate, the different parameters of Thomas model can be depicted with the help of the plot between ln $[(C_0/C_t)-1]$ and time **[77].**

3.12.2 THE ADAMS AND BOHART MODEL

This model was established for the study of the relationship existing between C_0/C_t versus time for the system which is continuous. It explains the starting part of the breakthrough curve and it also postulates that adsorption rate remains proportional to capacity of the resin as well as Cr^{+6} concentrations. The following expression for Adam-Bohart is given below;

$$\boldsymbol{t = (N_0 x/C_0 \gamma) - \left[\left(\ln\left(\frac{C_0}{C_t} - 1\right)/(C_0 k_{AB})\right)\right]} \qquad \textbf{…3.12.2(a)}$$

The linear equation of Adam-Bohart model is given by:

$$\boldsymbol{\ln\left(\frac{C_t}{C_0}\right) = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{F}} \qquad \textbf{…3.12.2(b)}$$

C_0 denotes Cr^{+6} concentration at inlet end and C_t in (mg/L) denotes outlet Cr^{+6} concentration at time t in (min); k_{AB} (L/mg.min) denotes rate of constant of Adam-Bohart model; F in (cm/min) denotes linear velocity obtained by the division of the rate of flow by area of cross section; Z in (cm) stands for depth of the column bed; N_0 in (mg/ml) denotes the capacity of adsorption. The parameters k_{AB} N_0 are obtained from the plot between ln (C_t/C_0) and time from its intercept and slope of the plot.

3.12.3 YOON – NELSON MODEL

Yoon-Nelson's established a model which states that probability rate of the adsorbate being adsorbed and the adsorbent of the breakthrough relating to the adsorbate decreases. The linear expression in a single phase system can be given as

$$\boldsymbol{\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN} t - \tau k_{YN}} \qquad \textbf{…3.12.3(a)}$$

k_{YN} in (L/min) is constant rate of Yoon-Nelson Model, τ (min) denotes time needed to achieve 50% of total breakthrough curve and t denotes time required for collection of sample. The slope

k_{YN} and intercept -τ k_{YN} is obtained from plot between ln (C_t/ (C_0-C_t)) and t. the capacity of adsorption q_{0YN} can be found from the equation below:

$$q_{0YN} = q_{total}/X = C_0 Q\tau/1000X \quad \textbf{…3.12.3(b)}$$

Where C_0 is inlet Cr^{+6} concentrations; Q is flow rate and τ is the time for achieving 50% of breakthrough curve and X denotes weight of resin.

Chapter 4

RESULTS AND DISCUSSIONS

CHARACTERISATION STUDIES

4.1 CHARACTERISATION OF ADSORBENT

4.1.1 FTIR ANALYSIS

The surface chemistry of CHBA resin before and after adsorption of Cr^{+6} was compared. Functional groups that are identified include ester, ether, alcohol, and carboxylic acid and nitro groups. Functional groups with corresponding adsorption range have been given in the table below.

Table 4.1: FTIR analysis of (CHBA) resin before adsorption

Sl.no	Absorption Range	Functional groups	Types of Vibration
1	1243.82	Ester	C-O stretch
2	1142.40	Ester, ether	C-O stretch
3	1018.94	ester,ether,alcohol,carboxylic acid	C-O stretch

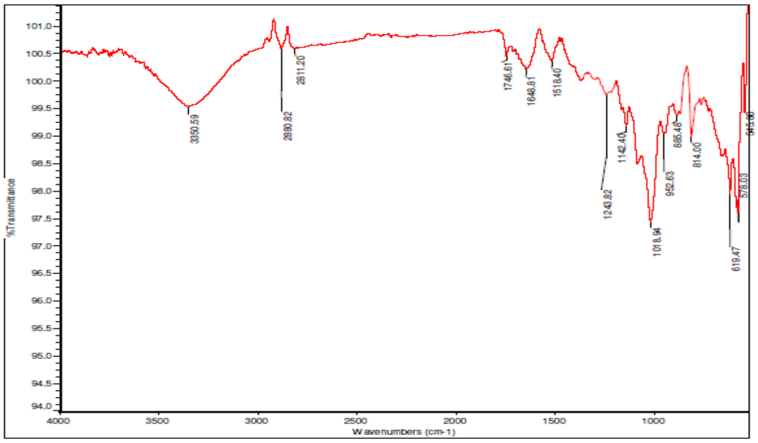


Figure 4.1: FTIR analysis without adsorption

Table 4.2: FTIR analysis of (CHBA) resin after Cr^{+6} adsorption

Sl. No	Absorption range	Functional groups	Types of Vibrations
1	1373.84	Nitro groups	N=0 Bond
2	1143.49	Ester and ether	C-O Stretch
3	1087.84	Ester and ether	C-O Stretch
4	1054.74	Ester and ether	C-O Stretch
5	1025.40	Ester and ether	C-O Stretch

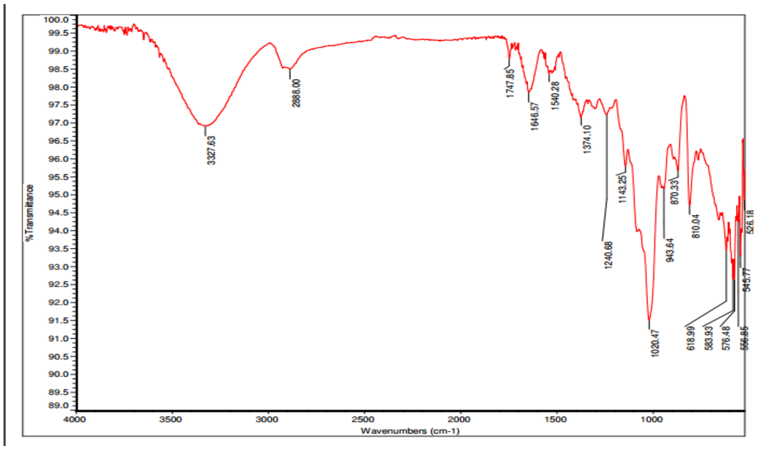


Figure 4.2 FTIR analysis of (CHBA) resin with adsorption

Infra red spectroscopy analysis is based on interactions between electromagnetic radiation and a compound. The atoms present in the molecules of that compound vibrate at natural frequencies lying in the range 1013-1014 cycles per second. This range covers Infra red radiations so these vibrations which results in dipole moment causes the absorption of Infra red radiations. When the radiation absorbed by the substance is plotted against incident wavelength, a graph is obtained which shows the presence of chemical bonds. FTIR hence is proficient in determining structures.

The FTIR spectrum of cassia gum powder without adsorption shows a broadband in the region 3700-3200 cm^{-1} which corresponds to –OH stretching, as hydrogen bonds can be stretched easily, therefore less energy is needed which makes the peak broader. The peak at $2880.82 cm^{-1}$ is attributed to C-H stretching vibrations; a strong and a sharp peak at $1648.81 cm^{-1}$ is due to –OH bending. A strong peak at 1243.82 -1018.94 cm^{-1} denotes C-O stretching vibration. In the graph, the area which are empty or without peaks shows that photons have not been absorbed at the corresponding frequency and confirms the absence of specific bond at that frequency. The FTIR spectrum of cassia gum powder is depicted in Figure 4.1.

The FTIR spectrum of Cassia-4-hydroxy benzoic acid resin shows a peak at 3100-3000 cm^{-1} which is attributed to C-H stretching vibration in aromatic nuclei. A strong peak in the region 1240.68-1020.47 cm^{-1} denotes C-O stretching vibrations. The peak at 1373.84 cm^{-1} shows N=O stretching vibrations . The peaks at 1143.49-1054.74 shows C-O stretching vibrations. The peak at 1518 cm^{-1} confirms the presence of aromatic ring. The zone from 2300 to 2100 cm^{-1} represents the alkyne triple bonds and nitrile triple bonds.The spectral peaks for polysaccharides are generally observed in the region 3700-3200 cm^{-1} due to –OH stretching frequency. The FTIR spectrum of Cassia 4-hydroxy -benzoic acid resin is depicted in Figure 4.2.

4.2 ELEMENTAL ANALYSIS

The resulting effects of the elemental analysis based on the Cassia 4-hydroxy benzoic acid resin (CHBA) is shown in the table below.

Table 4.3: CHNS ANALYSIS

Element	C	H	S	N
Theoretically Analysed	72.26	3.998	0.182	1.888
Percentage Analysed	70.17	3.771	0.174	1.600

An elemental analyzer consisting of model 1160 Carlo erba was used to find the different percentage of components present in the synthesized adsorbent. The analysis which was obtained was calculated Theoretically as (%) 72.26 (Carbon); 3.998 (Hydrogen); and 1.888 (Nitrogen), and analyzed to be (%) 70.17(Carbon); 3.771 (Hydrogen); and 1.600 (Nitrogen). The Theoretical and Percentage analyzed values are closer to each other which prove to be in worthy agreement.

4.3 NITROGEN CONTENT

Nitrogen content – calculated as follows:
Resin amount required = 1 g
Volume of 0.05 N HCl consumed = 3.2ml
Nitrogen content present in resin sample = 1.600 x 3.2 = 5.12mg/1g of resin
% of Nitrogen content = 5.12 %

4.4 ION-EXCHANGE CAPACITY

Standardization of NaOH solution

Mass CHBA resin (grams)	Volume of NaOH (mL)	Normality of NaOH	Average Normality of NaOH
0.5122	25.05	0.1014	
0.5121	25.00	0.1015	0.1015
0.5124	24.95	0.1016	

Exchange Capacity data:

Mass of resin used (grams, air dried) =1 g

mL NaOH used to titrate=25.05

Normality NaOH=0.1015

Calculation: Exchange Capacity $=\frac{mL_{NaOH \times N_{NaOH}}}{mass_{resin}}$

$= (25.05 \times 0.1015)/1$

$= 2.54$ meq/g

Similar results have also been obtained by **Feng-Bing Lian *et al* [78]; with** an ion-exchange capacity of 4.1 m mol g^{-1}.

4.5 MOISTURE CONTENT

Moisture content– calculated as follows:

The weight of dry resin = 0.9388 g

Weight of moisture = 1-0.9388 = 0.0612 g

% moisture content = 0.0612 x 100 = 6.12%

4.6 BATCH ADSORPTION STUDIES

4.6.1 EFFECT OF PARAMETERS

4.6.1.1 EFFECT OF ADSORBENT DOSE

The effect of CHBA resin dosage on the surface of Cr^{+6} is shown in the Figure 4.3. Different Resin dosages were varied from 0.1 g – 1g and other optimum factors were kept constant (at pH- 6.7, Initial Cr^{+6} concentration of 2 ppm, temperature- 30ºC, RPM - 130). The effects shows that the capacity of adsorption on CHBA resins gradually increased with increase of adsorbent dose from 0.1 g – 1g.with the increase in the resin amount, the adsorption sites also increases at higher concentration of the resin which results in higher removal of Cr^{+6} ions. If the adsorbent amount is increased at definite Cr^{+6} concentration, then adsorption capacity q_e (quantity of Cr^{+6} getting adsorbed on the surface per unit mass of resin) decreases because of the accessibility of less Cr^{+6} ions being available per unit mass of resin. Similar behavior has been reported for adsorption of Cr^{6+} on Diaion SA20A exchange resin (F.H.G.Mesbah ***et al***; 2010) **[79].**

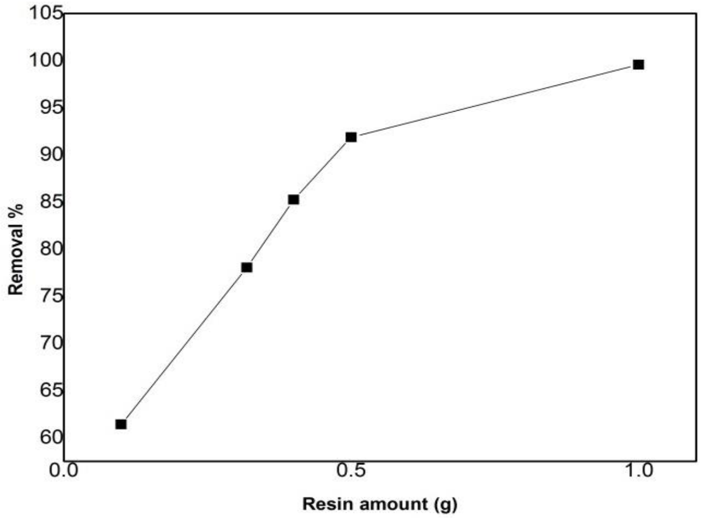


Figure 4.3: Effect of Resin dosage on % removal

4.6.1.2 EFFECT OF pH

pH of any element is said to be an essential constraint for the metal ions to get adsorbed on the surface as the metal ions solubility gets hindered by the factor pH, it also has an impact on the functional groups present in the adsorbent by hindering the counter ions concentration as well as the amount of ionization is also effected throughout the reaction. The pH was varied from 3 to 11 as given in Figure 4.4 in order to investigate the deviation in percentage removal of Cr^{+6} ions versus pH. Figure 4.4 depicts that the percentage removal of Cr^{+6} ions on the CHBA resin increases over pH ranging from 3 - 7, beyond pH 7 there is a decrease in % removal of Cr^{+6} till pH 11.During low pH, the external surface of the resin was completely shielded with H_3O^+ ions that participate effectively with Cr^{+6} ions for the vacant sites of adsorption. As the pH increases, there is a decrease in the concentration of H_3O^+ ions, resulting in the Cr^{+6} adsorption with the help of the resin. Various studies conducted with resins shows different optimum pH, where maximum removal of Cr^{+6} could occur (M.A Barakat ***et al***; 2013**)[80]**

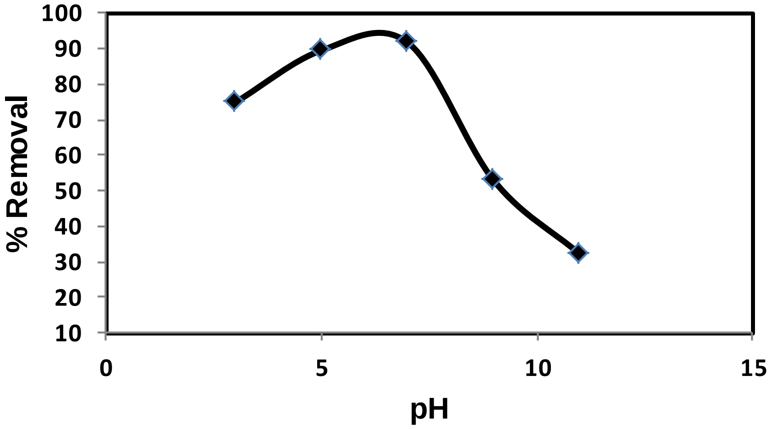


Figure 4.4 Effect of pH on % removal

4.6.1.3 EFFECT OF CONTACT TIME

Contact time study suggests the maximum time needed for a resin to achieve its equilibrium. The present trend is in agreement with previous studies. It is clear from Figure 4.5 which reveals that as the time increases varying from 10 - 30 minutes, the percentage removal of the Cr^{+6} ions also increases and the maximum time taken for the complete adsorption process to take place was around 25 min keeping the other factors as constant such as solution pH and speed of the shaker and temperature at 30ºC. It could be attributed to the fact that with the increase in time, the contact between the Cr^{+6} ions and surface of the resin increases or they gets more time that leads to more adsorption as the sites of adsorption is still incomplete.

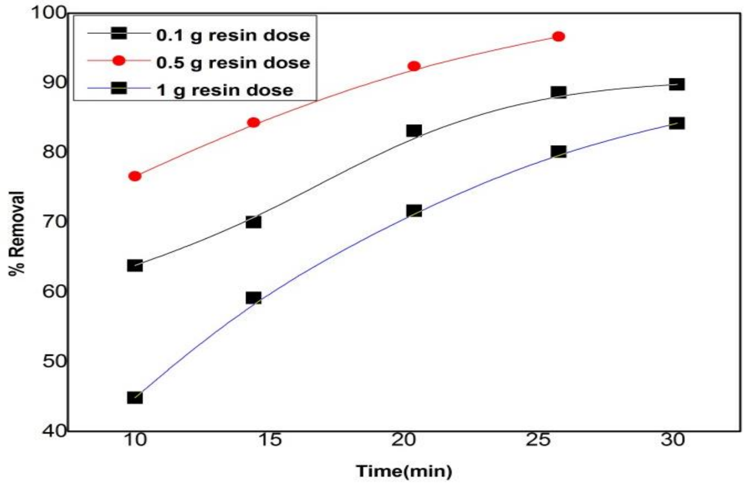


Figure 4.5 Effect of contact time on % removal

Once these sites are filled no more adsorption occurs although the contact time is increased which suggests that equilibrium is achieved. Hence to unnecessarily conduct the experiment beyond the equilibrium point it is essential to note the optimum contact time for all the adsorbents for each adsorption process. Moreover in this particular case, higher presence of functional groups like COOH groups, ester as well as ether groups on the CHBA resin surface helps to interact with the Cr^{+6} ions that results in better adsorption. Optimum time parameter is very important for an effective treatment of wastewater **[79, 80].**

4.6.1.4 EFFECT OF Cr^{+6} CONCENTRATION

Figure 4.6 shows the change in percentage removal of Cr^{+6} ions by varying the initial Cr^{+6} concentration from (3- 9 ppm) and by keeping the other parameters as constant(at pH- 6.7, amount of resin- 1g, temperature 30ºC, RPM 130). The adsorption behavior in Figure-5.6 clearly indicates the decreasing trend of Cr^{+6} adsorption on CHBA resin as the initial Cr^{+6} concentrations increased from 3-9 ppm. This is because of the increasing number of Cr^{+6} ions with a constant resin amount of 1 g .The percentage removal of Cr^{+6} becomes high at the initial stage because the area surrounding the resin is large enough for the Cr^{+6} adsorption to take place. Once saturation point is reached the resin capacity gets exhaust and adsorption rate is controlled by the Cr^{+6} ions, travelling from the outer surface of resin to the inner sites of the resin. Similar behavior has been reported for adsorption of Cr^{+6} on coffee based resins at varying pH (Khudbudin Mulani ***et al***; 2013**) [81]**

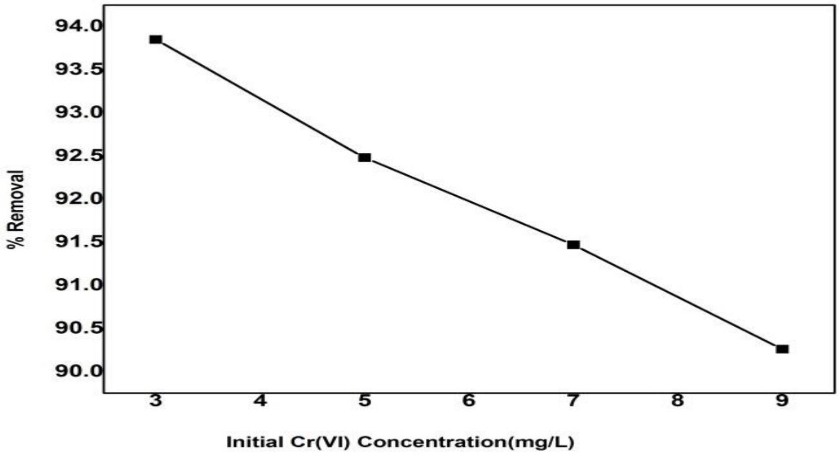


Figure 4.6 Effect of Initial concentrations on % removal

4.6.1.5 ADSORPTION ISOTHERMS

The results obtained from the adsorption experiments conducted at 30ºC are fitted to Freundlich, Langmuir, Temkin D-R isotherm models. The data related to adsorption were applied to linear form of Freundlich plot for different adsorbent dosage 0.1, 0.5 g and 1g as shown in the Figure 4.7, 4.8, 4.9 respectively. The higher R^2 value (>0.989) shows good agreement to Freundlich equation as depicted in the table 4.4. n value >1 was observed for all adsorbent dosages that indicates favorable adsorption process.

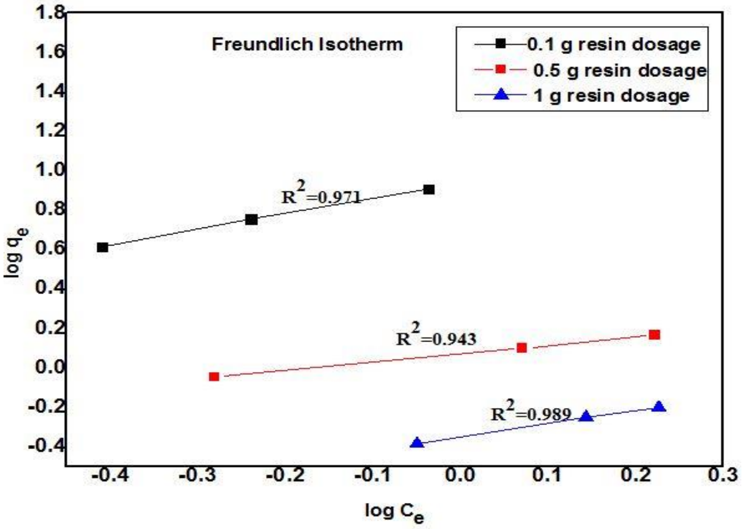


Figure 4.7 Freundlich adsorption Isotherm for Cr^{+6} on CHBA resin of 0.1 g, 0.5 g and 1 g resin

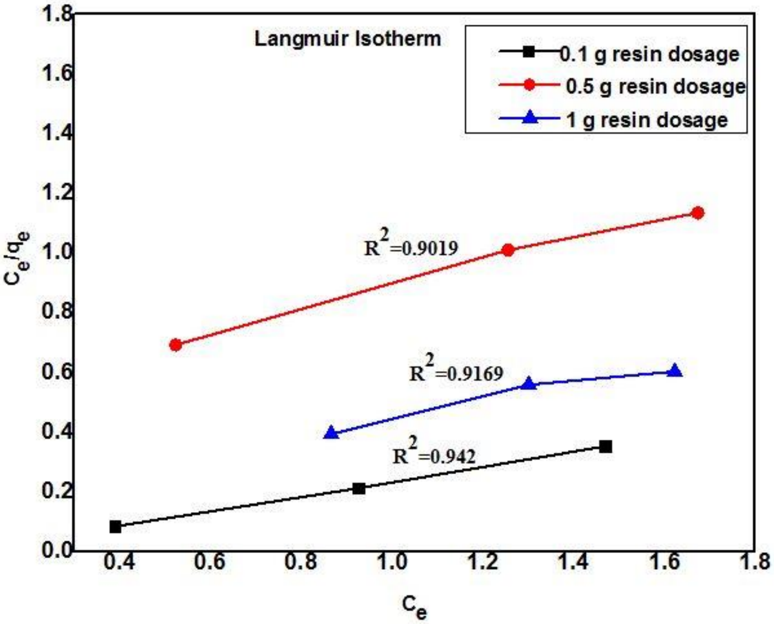


Figure 4.8: Langmuir adsorption Isotherm for Cr^{+6} on CHBA resin of 0.1 g, 0.5 g and 1 g.

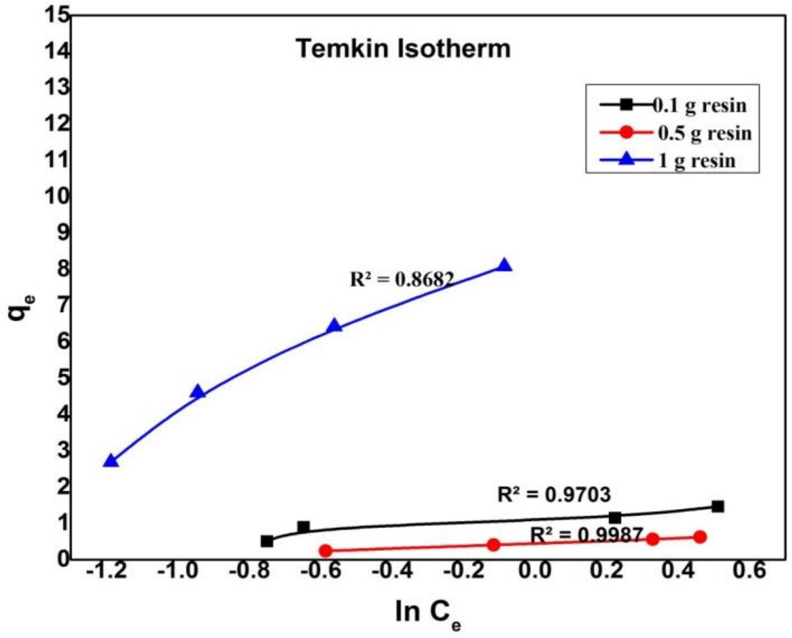


Figure 4.9: Temkin adsorption Isotherm for Cr^{+6} on CHBA resin of 0.1 g-1 g.

In Temkin model too the constants obtained from the Figure 4.9 shows as adsorbent dosage increased beyond 0.5 g, the k_T and B_1 constants increased. Moreover except for 0.5 g R^2 values observed as in table 1 shows good agreement to experimental data.

The same data when fitted to D-R model did not show good agreement as R^2 value reported for all the adsorbent dosages were < 0.9. The Process of adsorption follows chemical ion exchange since the value of E is less than 8 kJ/mol.

Table 4.4 Isotherm Parameters for the removal of Cr^{+6} using CHBA resin at different resin dosages

Equations	**Parameters**				
Freundlich	**Resin Dosages**	**0.1 g**	**0.5g**	**1g**	**1.5g**
	Kf	2.60	1.04	0.70	0.56
	N	1.38	1.46	1.59	1.87
	R^2	0.9711	0.943	0.989	0.9762
Langmuir	**Resin Dosages**	**0.1 g**	**0.5 g**	**1 g**	**1.5 g**
	q_m	18.14	2.072	1.40	0.54
	K_L	0.89	1.24	0.48	0.23
	R_L	0.272	0.138	0.229	0.325

	R^2	0.942	0.901	0.0916	0.929
Dubinin Radushkevih	**Resin Dosages**	**0.1 g**	**0.5 g**	**1 g**	**1.5 g**
	q_s	42.23	48.67	53.27	59.81
	E	0.380	0.381	0.412	0.513
	R^2	0.86	0.85	0.87	0.88
Temkin	**Resin Dosages**	**0.1 g**	**0.5g**	**1g**	**1.5 g**
	K_T	0.66	0.61	0.82	0.87
	B_1	1.9512	1.4415	2.8087	3.2215
	R^2	0.97	0.86	0.987	0.868

4.6.1.6 KINETIC STUDIES

To evaluate the sorption dynamics, consideration of kinetics and equilibrium studies is essential. The uptake rate which governs contact time can only be explained through kinetic studies. Numerous kinetic models, currently practiced to describe the process of adsorption and its mechanism involving first order Pseudo model, second order Pseudo model, intra-particle diffusion and elovich model. The experiment obtained at different concentration of Cr^{+6} (3 mg/L, 5 mg/L, 7 mg/L, 9 mg/L) has been fitted to each models as per Figures 4.8, 4.9, 4.10, 4.11 respectively. The constants obtained from individual plots have been represented in Table 4.5. It can be clearly seen that the data obtained from the experiment being conducted is found to be nearly fitting to second order Pseudo model equation, where R^2 suggest that equilibrium is obtained using resin for Cr^{+6} adsorption at a very faster rate and thereafter it remains constant.

The adsorption kinetics were calculated with varying time from 1-30 minutes. The data obtained from the conducted experiment was allowed to fit to Pseudo first order kinetic model as well as Pseudo second order kinetic model (Figure-4.10 & Figure -4.11). The greater R^2(0.99) value proves that the second order model was fitted well. Hence, removal of Cr^{+6} ions on the surface of resin was found to be feasible to second order pseudo model as comparatively to the first order Pseudo model**[82].**

The values of q_e obtained from the experiment and the values of q_e calculated from second order pseudo kinetic model are found to be closer to one another.

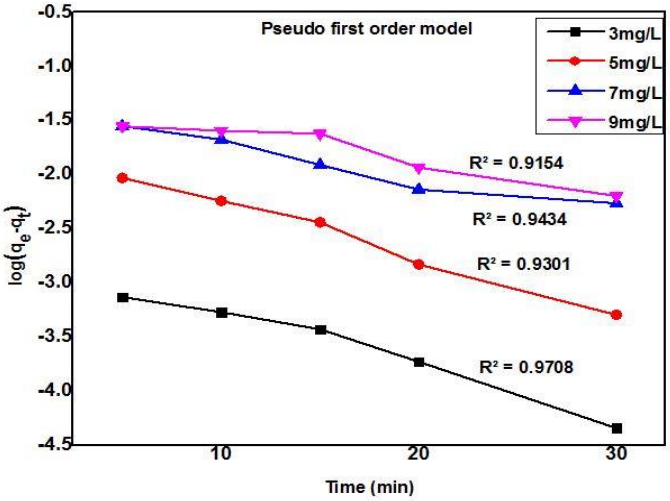


Figure 4.10 Pseudo first order kinetics at different concentrations

K_s value Vs 1/T was plotted the value of ln K_s has a good linear relationship with 1/T and the value of regression coefficient, R^2 is 0.99.The equation can be written as:

$$\ln \boldsymbol{K_s} = \boldsymbol{m}\frac{\boldsymbol{1}}{\boldsymbol{T}} + \boldsymbol{C} \qquad \text{...7.1(a)}$$

The logarithmic form of Arrhenius equation can be stated as:

$$\ln \boldsymbol{K_s} = -\frac{\boldsymbol{Ea}}{\boldsymbol{RT}} + \ln \boldsymbol{A} \qquad \text{...7.1(b)}$$

Comparing equation (7.1) to (7.2) we get the slope as E_a/R =m thus E_a and is calculated as 4.28 KJ/mol.

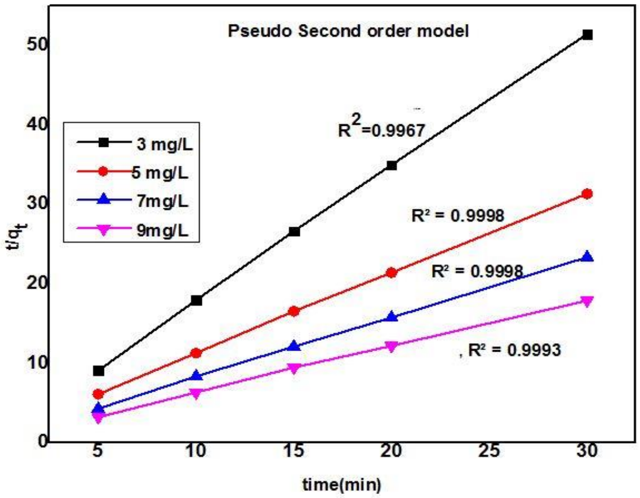


Figure 4.11 Pseudo second order kinetics at different concentrations

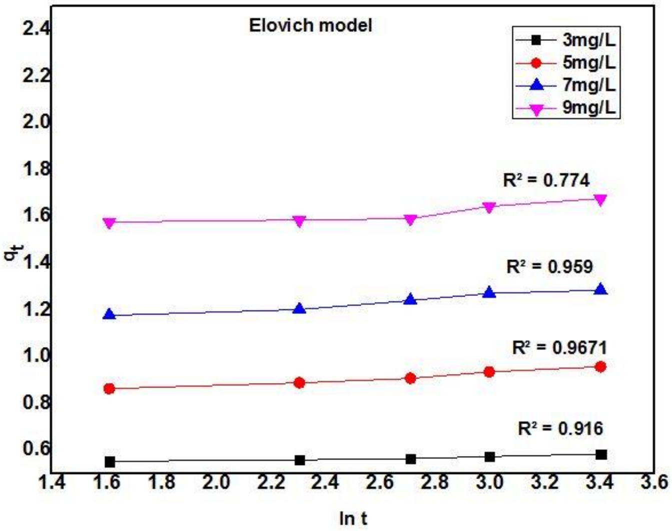


Figure 4.12: Elovich model at different concentrations

The initial adsorption constant, a, and b defined as constant of desorption, can be obtained from plots between q_t and ln t (Figure-4.12). Table - 4.5 lists the Constants present in the Elovich equation. The constants a and b varies linearly with the Cr^{+6} concentration.as a function of the initial solution concentration. Thus with the increase in the concentration varying from 3 mg/L- 9 mg/L, the constant b decreases from 59.52 to 16.213 g/mg because of the low surface being available for adsorption of Cr^{+6} ions. If there is an increase in the solution concentration ranging from 3 to 5 mg/L, the value for constant a also got increased from 1.22×10^5 to 2.53×10^4 mg/g min which predicts there is an increasing trend in adsorption process while decreasing trend in desorption process as the concentration of the solution is increased. However at a higher concentration of (9 mg/L), the obtained R^2 value is very poor.

In Intra-particle diffusion study k_{id} values were calculated by the plots between q_t and $t^{1/2}$ in (Figure-4.13) and corresponding values are in Table 4.5. The process follows pore diffusion. with the increase in Cr^{+6} concentration from 3 mg/L to 7 mg/L the values of R^2 also increases suggesting this model is fitting to the experimental data well till 7 mg/L initial Cr^{+6} concentration.

Table 4.5: Kinetic Parameters for the removal of Cr^{+6} using CHBA resin at different Concentrations

Equations	Parameters				
Pseudo-first order	**Concentration**	**3mg/L**	**5mg/L**	**7mg/L**	**9mg/L**
	q_e exp(mg g^{-1})	0.5958	0.994	1.388	1.7882
	q_e cal(mg g^{-1})	0.62	1.10	1.52	1.84
	K_f	0.3286	0.4669	0.6791	0.3358
	R^2	0.9708	0.9301	0.9434	0.9154
Pseudo-second order	**Concentration**	**3mg/L**	**5mg/L**	**7mg/L**	**9mg/L**
	q_e exp(mg g^{-1})	0.5958	0.994	1.388	1.7882
	q_e cal(mg g^{-1})	0.5963	0.9957	1.3912	1.7898
	K_s	244.55	83.35	72.77	66.41
	R^2	0.9997	0.9998	0.9998	0.9993
Intra-particle diffusion	**Concentration**	**3mg/L**	**5mg/L**	**7mg/L**	**9mg/L**
	K_{id}	0.0096	0.0299	0.0358	0.0328
	C	0.5286	0.795	1.0976	1.488
	R^2	0.975	0.989	0.957	0.864
Elovich	**Concentration**	**3mg/L**	**5mg/L**	**7mg/L**	**9mg/L**
	a(mg/g min)	$1.22*10^5$	$1.47*10^2$	$3.77*10^2$	$2.53*10^4$
	b(g mg^{-1})	59.52	18.72	17.8571	16.213
	R^2	0.916	0.96	0.959	0.774

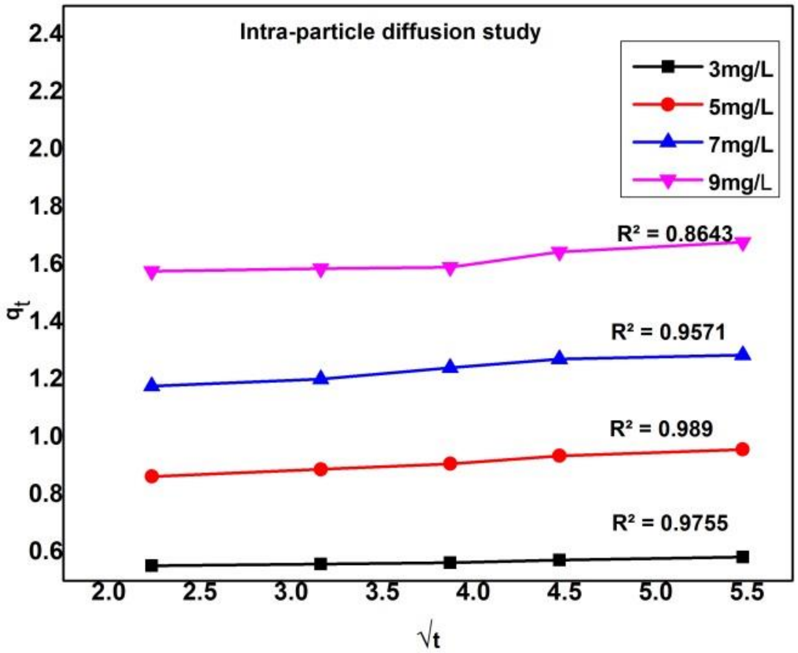


Figure 4.13: Intra-particle diffusion study at different concentrations

4.6.1.7 THERMODYNAMICS STUDY

The plots made between ln K_L and 1/T was found to be as a straight line (Figure - 4.14) and the slope, intercept from the corresponding plots obtained in the graph is considered for the calculation of the enthalpy and entropy of the system and values are represented in the following table 4.6. values of ΔH was obtained as 21.48 KJ and ΔS was obtained as 68.98KJ/mol. The ΔG value decreases from 17.87 to 2.88 kJ/mol with the increase in temperature varying from 20 to 30ºC which suggests that there will be greater number of Cr^{+6} species as increase in temperature. The Positive values of change in enthalpy shows that there is an presence of an energy barrier during the process of adsorption and the process of adsorption follows process of endothermic reaction. The positive values in the change of entropy (ΔS) shows good binding capacity of Cr^{+6} ions for the resin surface and it also increases the uncertainty of the solid solution interaction during the process of adsorption.

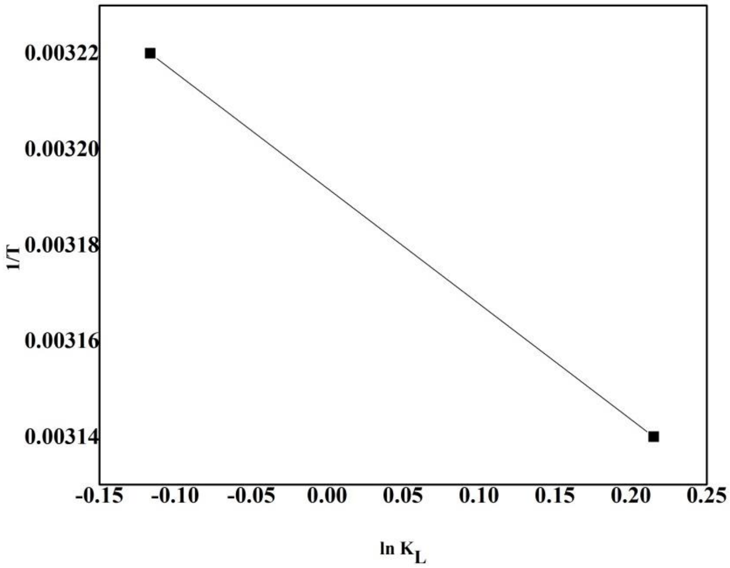


Figure 4.14 Vant Hoff plot for the adsorption of Cr^{+6} at various temperatures

Table 4.6: Thermodynamic Parameters values for the adsorption of resin on Cr^{+6} at different temperatures

T(Kelvin)	ΔH^o(kJ/mol)	ΔS°(J/mol K)	ΔG(KJ/mol)
293	21.48.	68.98	17.87
298	21.48.	68.98	5.416
303	21.48.	68.98	2.887

Chapter 5

BATCH STUDY- DESIGN OF EXPERIMENTS

RSM is a technique which relates to a plan of Scientific and statistical systems which have been utilized for the demonstration and investigation of a procedure which is affected by various mathematical variables. A model in a RSM method allows to identify the impacts of interactions on various process parameters, effects related to high order and emphasize on getting greatest wanted response by deciding the conditions on which the model has to be operated. **[83]**

A Box-Behnken Design (BBD) method employed from RSM has been explored in the investigation to make use of the mathematical variables for removal of Cr^{+6} ions from drinking water by batch process .The design model used during the experiment was BBD which consists of three variables (Initial concentration, Resin dosage, pH), each of them with minimum as well as maximum levels. The advantage of the model is that it is used to simplify the complex response function by using few combinations of variables **[84]**. 15 experiments were required to determine 10 coefficients of second order polynomial equation. Initial Cr^{+6} concentration were taken as (3-9mg/L), pH (3-9) and resin dosage (0.3-0.9g) were taken as input variables. The response of the system was expressed by percentage removal. The experimental table 5.1 represents the experimental design matrix derived from BBD. 3 major steps involved in optimization process statistically designing experiments coefficients estimation, response estimation to check the adequacy of the design model. Y= f (A, B, C…An), where Y is the response of the system and A, B, C are the variables which is called as factors. (Annadurai G. **et al;** 2000).Table 5.1 shows the experimental range for each factor used and defined in three level (low, basal and high) coded as (-1, 0, +1).

Table 5.1: Coded and actual values of variables of the experimental design.

Variable	Factors	Range and level		
		Level(-1)	Level (0)	Level(+1)

pH	A	3	6	9
Dosage of adsorbent	B	0.3	0.6	0.9
Initial Concentration	C	3	6	9

5.1 RESULTS AND DISCUSSIONS

5.1.1 STATISTICAL ANALYSIS

About 15 experiments were examined in distinct arrangements of the constraints to report the outcome of three factors such as Resin dosage, initial concentration, and pH (Table 5.1). It shows that the predicted and experimental data are related to percentage removals of $Cr^{+6.}$

The experimental Model data's were well fitted to Response Surface Methodology (RSM). [Table 5.1] and a second order quadratic polynomial equation was derived from the variables. The equation was presented in equation –8.1.1 (a) below, where Y is represented as the yield of experiment, A is the resin dosage, B denotes pH and C represents as initial concentration.

$$\mathbf{Y = 93.38 + 0.75 \times A - 2.33 \times B - 11.01 \times C - 1.37 \times AB - 1.2 \times AC + 0.19 \times BC - 2.18 \times A^2 - 5.38 \times B^2 - 9.27 \times C^2} \qquad \ldots 8.1.1\ (a)$$

Table 5.6 shows the ANOVA for the response. Regression equation determines the major changes in response of the values and greater F value implies the best suited model. The corresponding values of p are less than 0.05 signifies the model is substantially significant. (Paritosh tripathi *et al*; 2009)**[85]**

Adequacy of models is checked to illustrate the percentage removal of Cr^{+6} . The model tests adequacy were carried out and the outcomes are illustrated in Table 5.3 Results obtained shows that the p-value for the quadratic model is less than 0.05 and the R^2 for the quadratic model is found to be highest as compared with other models. Link between independent variables and amount for Cr^{+6} removals was preferably demonstrated using a quadratic model.

Normality of residuals was examined from the data's achieved. The normal probability plot or dot diagram of the residuals was plotted as shown in Figure 5.1. Data points obtained were found close to the straight line which proves that the chosen model adequately fits for Cr^{+6} removals.

The obtained F-values and p value of the model for determining the percentage removal of Cr^{+6} is shown in the Table 5.2. The F value is 78.18 with p-value is <0.05 indicating model expressions are substantial, whereas p greater than 0.1000 indicates models are not significant, as shown in the table 5.3. The coefficient of determination (R^2) and adjusted R^2 of this model were 0.9901 and 0.9775, respectively. The coefficient of determination (R^2) is 0.9901 suggesting that 99.01% of the inconsistency in percentage removal of Cr^{+6} can be described by this model. Regression also offers a technique to estimate the nature and the degree of correlation among dependent and independent variables. If the R^2 value is nearer to 1.00, the model will be the strongest one as well the response predictions will also be improved. The variances between values of R^2 (0.9901) and adj. R^2 (0.9775) are minor; as a result, the resemblance between R^2 and adjusted R^2 shows the capability of the model to predict the response.

Lack of fit F-value of 3.09 with p>0.05 implied that the lack of fit was not significant in relative to pure error. A non-significant lack of fit is desired for fitting the model. Thus, a well-fitted model was obtained for the equation of percentage removal.

Table 5.2: Experimental and the predicted values yields for removing Cr^{+6}

Run	Resin dosage (A)	pH(B)	Initial Concentration(C)	Response (Adsorption %)	
				Y experimented	Y Predicted
1	0.9	6	9	70.23	72.32
2	0.6	6	6	93.38	93.46
3	0.3	6	3	91.18	92.04
4	0.9	6	3	93.85	94.233
5	0.3	9	6	82.3	82.52
6	0.6	6	6	93.38	93.46
7	0.6	6	6	93.38	93.46
8	0.6	9	9	66.32	67.2
9	0.6	6	6	93.38	93.46
10	0.6	3	9	68.27	69.19
11	0.9	3	6	92.09	93.21
12	0.6	3	3	91.51	91.89
13	0.6	9	3	88.82	89.93

14	0.3	6	9	72.45	73.36
15	0.6	6	6	93.38	94.28
16	0.9	9	6	82.34	83.46
17	0.3	3	6	86.56	87.23

5.1.2 MODEL ADEQUACY

We must consider two-way interactions such as three-factor complexed system. Statistical data were fitted to models such as Linear, interactive, quadratic and cubic to achieve the regression equations. The best suited model to characterize Cr^{+6} removal using CHBA resin were chosen by lack of fit test and model summary statistics as shown in table no-5.4 and 5.5, All $P > 0.05$ for lack of fit signifies the model does not fit the data .Cubic model was neglected whereas quadratic models was found to have maximum “R squared” and “Adjusted R-squared “values. All three terms (A, B, C) and three 2F1 term (AB,AC, BC) from ANOVA table shows values are significant at $p< 0.05$ and was found to be the most preferred model. As quadratic model comprises terms to build the whole model for calculating the response and produces minimum value of PRESS (predicted residual sum of squares), it indicates that the model can be used for comparative precision in predicting future consequences and thus, promotes further analysis **[86].**

Table 5.3. Adequacy of the model tested

Source	Sum of Squares	Df	Mean square	F-value	P-value Prob>F	Remarks
Mean versus Total	112400.56	1	112400.56			
Linear versus Mean	1017.99	3	339.33	7.68	0.0033	
2F1 versus linear	13.65	3	4.55	0.081	0.9688	
Quadratic versus 2 F1	545.24	3	181.75	81.10	<0.0001	Suggested
Cubic versus quadratic	15.69	3	5.23			Aliased
Residual	0.0000	4	0.000			

Total	125800.5	17	7397.09

Table 5.4: Lack of Fit Tests

Source	Sum of Squares	Df	F values	P- values Prob>F	Remarks
Linear	574.58	9	16.13	0.0063	
2F1	560.93	6	0.26	0.9392	
Quadratic	15.69	3	49.35	0.0004	Suggested
Cubic	0.0000	0			Aliased
Pure Error	0.0000	4			

Table 5.5: Model Summary Statistics

Source	Std.Dev	R-Squared	Adjusted R-squared	Predicted R-Squared	PRESS	Remarks
Linear	6.65	0.6392	0.5560	0.4347	900.29	
2 F1	7.49	0.6478	0.4365	-0.0201	1624.63	
Quadratic	1.50	0.9901	0.9775	0.8424	251.01	Suggested
Cubic	0.0000	1.0000	1.0000		+	Aliased

5.1.3 FITTING OF SECOND-ORDER POLYNOMIAL EQUATION AND STATISTICAL ANALYSIS

As shows in Table 5.6, the ANOVA shows that quadratic effects of initial concentration (C) and pH (B) were significant ($p<0.05$), while linear effect only initial concentration was significant ($p<0.05$). A $p< 0.05$ shows the model is significant whereas $p> 0.1000$ indicates shows insignificant models. F-value of 78.18 shows a significant model with only 0.01% chance of increment which could occur due to noise.

The resin dosage does not ensure an influence on the removal of Cr^{+6} removals. It may be due to the quantity between high and low limit of the resin dosage used in small range. The initial concentration has substantial effect on the removal of Cr^{+6}. The resin dose which is known as the low order interaction is mainly affected due to the high significance of the initial concentration of the Cr^{+6} solution**[87]** .The removal of Cr^{+6} by treating the cassia gum powder through the preparation of the (CHBA) resin was maximum at pH 6 which is the normal drinking water pH.

The initial concentration value of the Cr^{+6} solution shows an essential part during the overall a process of adsorption and mostly on adsorption capacity. As the initial concentration of the adsorption solution was increased, there is a larger removal with a higher ratio of available surface to initial Cr^{+6} concentrations but in cases of higher concentration, there is less Cr^{+6} removals. With decreased in pH of adsorbed solution, there is an attraction of positively charged functional groups near the reactive Cr^{+6} ions due to an increase in negative charges on the surfaces .(Santhy K, ***et al***; 2006)**[88]**

Table 5.6. ANOVA of the second-order polynomial equation

Source	**Sum of squares**	**Df**	**Mean square**	**F-value**	**Prob>F**	**Remarks**
Model	1576.88	9	175.21	78.18	<0.0001	Significant
A-Resin dosage	4.53	1	4.53	2.02	0.1981	
B-pH	43.48	1	43.48	19.40	0.0031	
C-Initial Concentration	969.98	1	969.98	432.81	<0.0001	
AB	7.54	1	7.54	3.36	0.1094	
AC	5.98	1	5.98	2.67	0.1464	
BC	0.14	1	0.14	0.061	0.8119	
A^2	20.01	1	20.01	8.93	0.0203	
B^2	121.76	1	121.76	54.33	0.0002	
C^2	362.02	1	362.02	161.53	<0.0001	
Residual	15.69	7	2.24			
Lack of Fit	15.69	3	5.23			
Pure error	0.0000	4	0.0000			

Moreover, the statistical analysis with standard deviation and mean are depicted in the table-5.5. The "Pred R-Squared" of 0.8424 is acceptable with an "Adj R-Squared" of 0.9775; i.e. the difference is less than 0.2. It was also observed that the "Adequate Precision" measures the signal to noise ratio. A desirable ratio should always be greater than 4. The ratio of 25.555 indicates an adequate signal which concludes that this model can be used for navigation of the design space.

5.1.4 MODEL VALIDATION

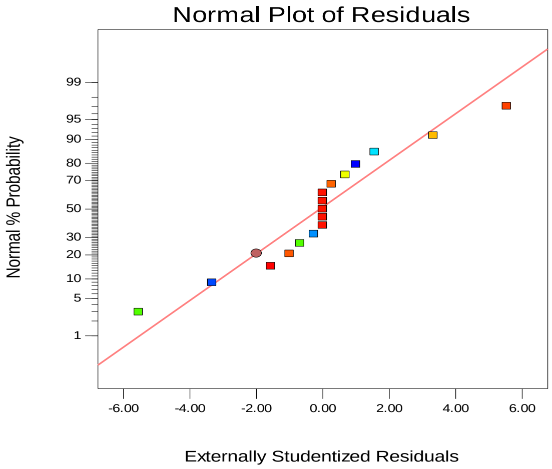


Figure 5.1: Normal probability plot of residuals for Defective percentage

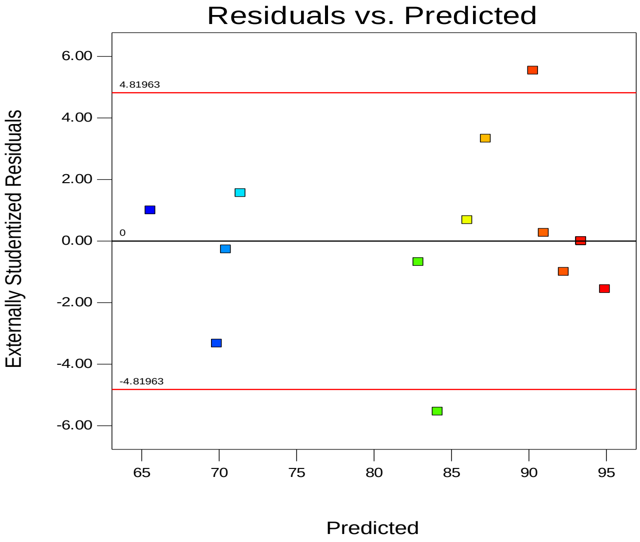


Figure 5.2. Residuals versus Predicted for Defective percentage

Main purpose of validation is for prediction and conformation of variable response by means of the optimal values related to process constraints. Figure 5.1 and Figure 5.2. Shows Normal probability plot of residuals for Defective percentage and Residuals versus Predicted for Defective percentage. Figure 5.1 show that residuals almost follow a straight line implicating that the errors were dispersed normally. Figure 5.2 show that the point does not follow a normal linear behavior. (Rathish Raghupathy, ***et al***; 2014)[**79**]

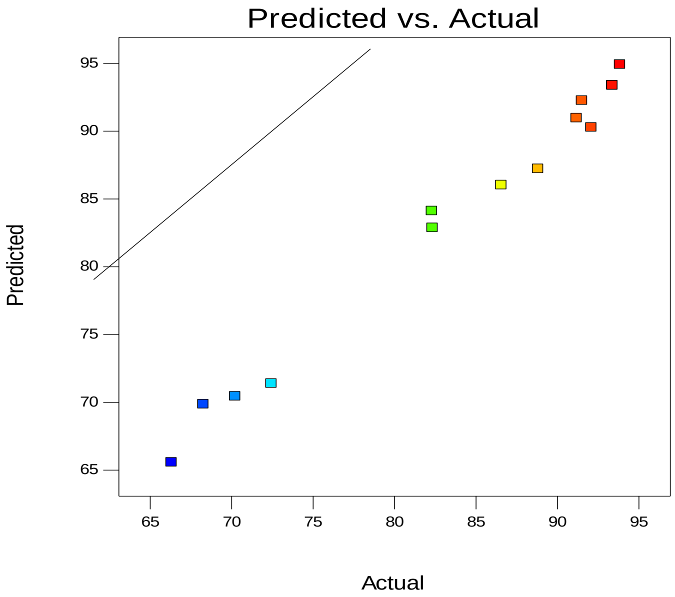


Figure 5.3: Scatter diagram of predicted response versus actual response of Cr^{+6} removals

Figure.5.1 shows a graph between experimental data in relation to predicted value for Cr^{+6} removals (%). It was found that experimental values lie close to the straight line that indicates a close correlation between the two. The points clustered in the parity plot (Figure 5.3) around the diagonal line shows good fit of model. Model employed is chosen since residuals for many of the responses are below 10 % and the residuals points lie close to the diagonal line. The different ideas are discussed from any points lying outside the red lines. It is evident from the Figures 5.1, 5.2 and 5.3 that all points line inside the red lines which confirms that the model fit well to the variables.

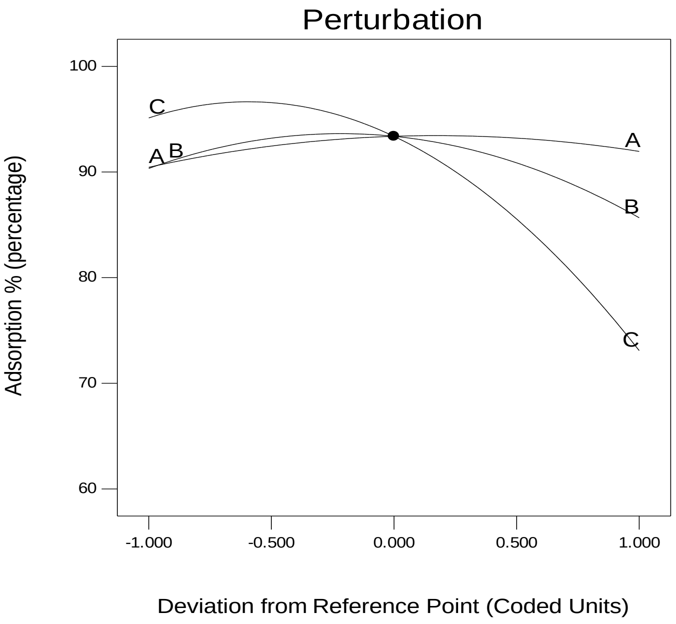


Figure 5.4: Perturbation Plot showing adsorption %

Perturbation plot of three independent factors is shown in Figure 5.4. The line A represents resin dosage which does not change much from the reference point indicates a lower significance with adsorption %. Much change can be found in line B (pH) and C (initial Cr^{+6} concentrations) with respect to reference points which shows the variables are significantly related to adsorption %.

5.1.5 INTERACTION EFFECT OF PROCESS PARAMETERS

To investigate the effect of the three parameters on the % adsorption of the resin, the response surface methodology was adopted, and three-dimensional diagrams were plotted. Based on the ANOVA results obtained both pH and initial concentration showed significant effects on the % adsorption whereas resin dosage showed the least effect. The quadratic effects of pH and initial concentration shows good fit whereas quadratic effects of resin dosage as well as the interaction effects of all three parameters were considered moderate. The response surface graphs of resin was shown in Figure- 5.5.

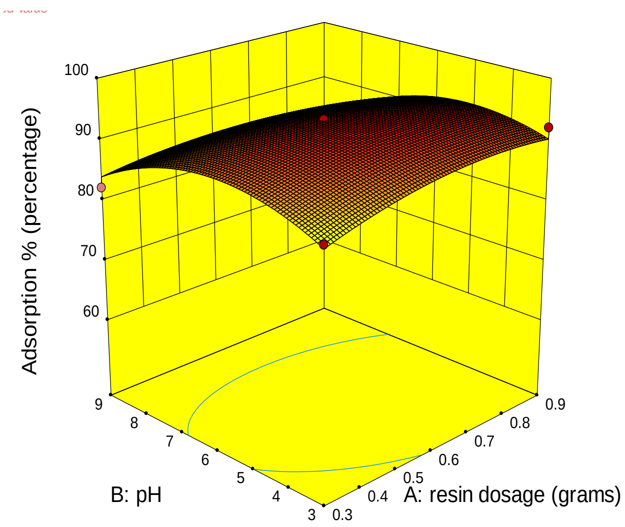


Figure 5.5: 3D response surface graph for Cr^{+6} removals versus adsorbent dose (g/L) and pH for Adsorption of CHBA resin

The combined effects of pH and resin dosage on the response are depicted as in the Figure 5.5.It was observed that % adsorption increased with the increasing resin dosage and pH of 6.13 at an initial Cr^{+6} concentrations of 4.53 mg/L. The reason behind this is that increase in amount of resin leads to an increase in the surface area of resin and due to the availability of greater number of adsorption sites for Cr^{+6} ions Figure 5.4 also indicates that the maximum adsorption (95.05%) occurs at a (pH 6.13) and an amount of resin dosage of 0.43 g, which proves to be in accordance with the model. Similar results were obtained by **Xinxi Zhang** using MIEX resin **[89].**

The interaction of AC with response to adsorption % is depicted in the Figure 5.6. The % adsorption increases with the increase in resin dosage and it was found that the % adsorption increases up to 4.53 mg/L and afterwards beyond 4.53 mg/L, it decreases. The decrease in the % adsorption is due to the splitting effect of the concentration gradient between the Cr^{+6} ions and the resin which causes a decrease in amount of Cr^{+6} adsorbed onto the unit weight of the resin. Similar results were obtained in the removal of nickel using hypnea valentiae by **M.Rajasimman[90]**

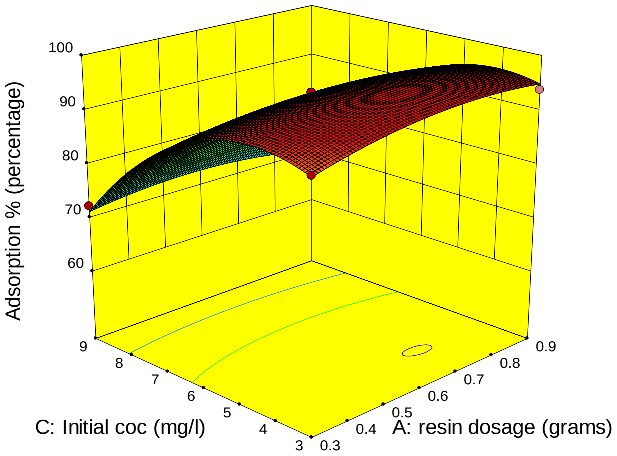


Figure 5.6: 3D response surface graph for Cr^{+6} removals versus adsorbent dose (g/L) and initial concentration for Adsorption of CHBA resin

The interaction of BC with response as adsorption % is depicted in Figure 5.7. Which can be explained as follows: with the increase in pH, the % adsorption increases slightly but at higher concentration of pH, the % adsorption decreases. But with the increase in initial concentration, the curve decreases and at lower initial concentration the % adsorption is maximum. But if both the factors were observed, then the maximum % adsorption occurs at pH of 6.12 while initial concentration at 4 ppm. The observations can conclude that among all the interactions (AB, BC, AC) initial concentration and pH mainly governed the % removal.

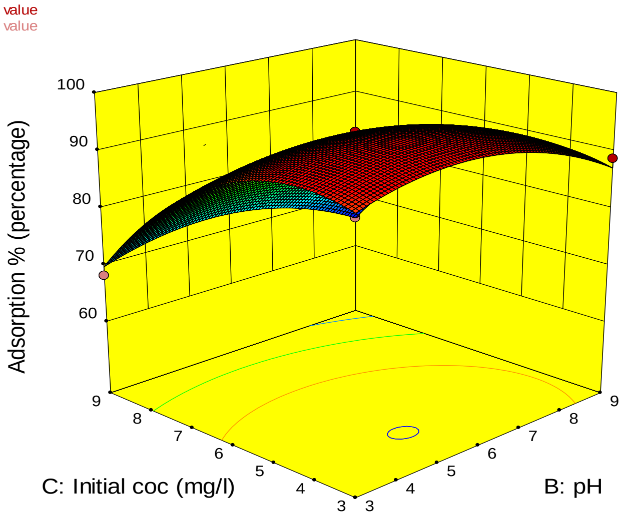


Figure 5.7: 3D response surface graph for Cr^{+6} removals versus adsorbent pH and initial concentration for Adsorption of CHBA resin

There is an increase in % Cr^{+6} removals with an increase in pH up to a maximum value of 6.45.This phenomenon can be explained by the functional groups involved in the Cr^{+6} binding mechanism. FTIR spectroscopic analysis revealed that ester, carboxylic and nitro groups participated actively in the adsorption of Cr^{+6} ions and the potential binding mechanism of functional groups depend on the initial pH of the solution. At pH 3-6, maximum number of interactions occurs between cations like Cr^{+6} and the possible functional groups present on CHBA resin due to electrostatic attraction. At pH=3,H^+ and H_30^+ ions increases and interference of these ions with Cr^{+6} for the binding sites due to electric repulsion may result in the decrease in the % removal of Cr^{+6} .Similar results were found by **R.Parathasarthy** in sorption of Zr^{+4} using Karanja Seed cake**[91].**

Table 5.7: optimum and confirmative values of process parameters for maximum removal efficiency

Optimal levels	Adsorbent Dose(g)	pH	Initial Concentration(mg/L)	Adsorption %
	0.434	6.13	4.53	95.05

Table 5.8 Data of Confirmation run

Run	Adsorbent dose (g)	pH	Initial Concentration (mg/L)	Y (% Removal)
1	0.434	6.13	4.53	95.05
2	0.434	6.13	4.53	94.26
3	0.434	6.13	4.53	93.82
4	0.434	6.13	4.53	94.65

Validation of the model

Adsorption % obtained from the optimal conditions for the removal of Cr^{+6} was maximum was achieved by the method of point prediction and response of plots as depicted in the table 5.7. The maximum optimal % adsorption was found to be 95.05 % at a resin dosage of 0.434 g, pH 6.13 at an initial concentration of 4.53 mg/L. Then, further another experiment was carried out using these optimal factors and the results are as shown in the Table 5.8. As the experimental values comes out to be closer to the predicted ones and p value<0.05 which proves that the results confirms the model validity.

Chapter 6

RESULTS AND DISCUSSION- COLUMN ADSORPTION

6.1 EFFECT OF PARAMETERS

6.1.1 EFFECT OF BED HEIGHT

Figure. 6.1 represents the curve of breakthrough that is acquired for removal of Cr^{+6} ions at various bed heights inside the column of 2, 4 and 6 cm, at a rate of flow of 3 ml/min which is kept as constant and Cr^{+6} concentration as 20 ppm. it was concluded that the time required to achieve the breakthrough curve as well as the time required by the column bed for complete exhaustion increases as the height of the bed increases providing greater adsorption sites. At a definite concentration of 20 mg/L, percentage removal of Cr^{+6} ions increases slowly ranging from 67.14% – 71.42%. However the maximum removal 94.23 % was reported for Cr^{+6} concentration of 5 ppm with a maximum height of bed as (6cm). With the increase in height of bed, percentage of removal of Cr^{+6} also increased because of the higher area being available at the surface of the resin and therefore due to this higher area there will be more vacant adsorption sites which will be available for the occurrence of the process of adsorption. Moreover, with the increase in height of bed, the Cr^{+6} ions gets chance of more contact time to interact with the resin which results in higher Cr^{+6} removal from the column bed.

The breakthrough curve was to some extent reduced with enhancement of the height of bed, which brought about broadened mass exchange zone. Similar behavior was also reported in column studies for heavy metal removal using macro fungus **[92]** Hence as the bed height increases, the operation of column was simultaneously improved and continued to reduce the resin concentration at the end of the system. The maximum the bed height, the less time will be required by the adsorbent for bed to exhaust resulting in operating the bed for larger time period without affecting the resin amount in the bed. Similar findings have been suggested during column studies for nitrate removal by resins.

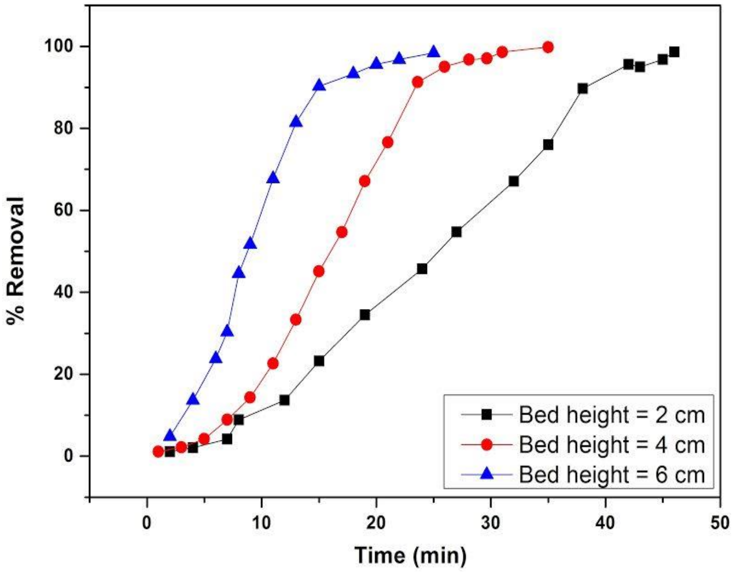


Figure 6.1: Effect of bed height

6.1.2 EFFECT OF SUPERFICIAL VELOCITY

The impact on the superficial velocity in the process of adsorption by resin was carried through keeping constant Cr^{+6} concentration of (20 mgL^{-1}), temp around (25ºC) and depth of bed as (6cm), at a constant pH of 6.7. The superficial velocity can be maintained with the help of peristaltic pump from 3 to 7$mLmin^{-1}$. When the flow velocity is minimum, the performance of column was better. [Figure-6.2]

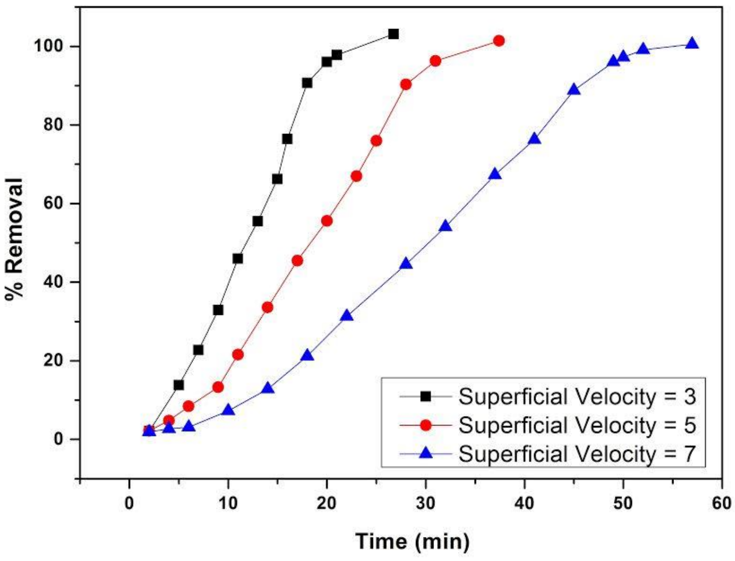


Figure 6.2: Effect of superficial velocity

When the flow velocity is low, the process of adsorption was very rapid initially because of the greater sites of adsorption so that the Cr^{+6} ions will be captured around the surface of the resin. During the next process, the Cr^{+6} ions as already being occupied by these sites, the capacity of uptake will be less. From the Figure- 6.2, the time required by initial breakthrough curve and the time required by the bed to get exhaust gives breakthrough curves as steeper as possible, as the flow velocity decreases from 3 - $7mLmin^{-1}$. The superficial velocity also has a strong impact on the Cr^{+6} adsorption capacity. With the increase in superficial velocity ranging from 3 - 7 $mLmin^{-1}$ the % removal decreases from 67.14% to 42.06% [Table 6.1.]. It is because of the insufficient contact time between the Cr^{+6} ions and the resin as the metal ions could not diffuse into the resin pores **[93].**

6.1.3 EFFECT OF INLET CONCENTRATION

The inlet Cr^{+6} concentrations have a strong effect on the curves of breakthrough at a definite bed depth as 6 cm with a constant rate of flow of 3ml/min is Figure 6.3. with the increase in Cr^{+6} concentration ranging from 5- 20mg/l, there is a slight reduction in the time of break point. While with the decrease in the initial Cr^{+6} concentrations, the steeper will be the curves of breakthrough and reduction of breakthrough volume also occurs. Contrary behavior have been reported by other authors where with increase in solute concentration, the breakthrough curve becomes steeper **[93,94].** With the decrease in concentration, the active sites of resin are sufficient enough to adsorb the cr^{+6} ions however with increase in concentration, the bed gets exhausted or saturated and hence the process becomes slow at higher concentrations.

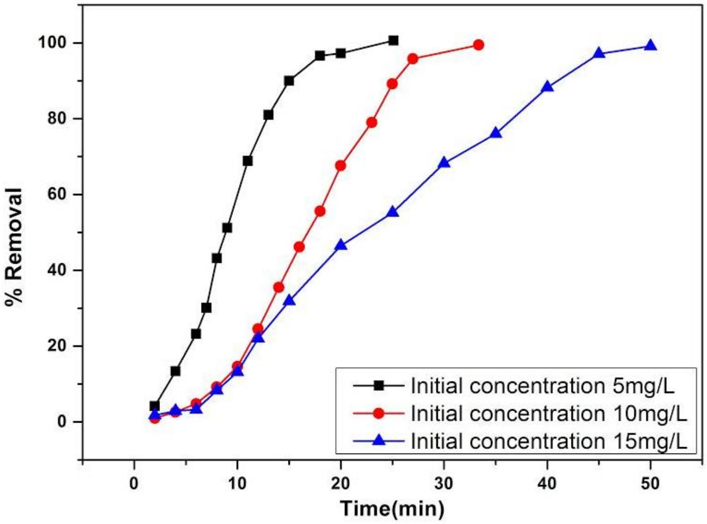


Figure 6.3: Effect of initial Cr^{+6} concentrations

6.2 REGENERATION STUDIES

The study is based on the reusability of the resin to understand the prospective capability of adsorption process. Therefore, resin regeneration plays a significant role during the improvement of commercial fields. Regeneration means Cr^{+6} removals from the resin surface. This process should produce Cr^{+6} concentration of less amount, without harming the resin capacity so that the resin can be further reused for different cycles of adsorption and desorption. During the regeneration study (Figure- 6.4), removal of Cr^{+6} was done with the help of 0.1N HCl at a rate of flow of $3mLmin^{-1}$ which is kept constant, and depth of the bed as 6cm along with $20mgL^{-1}$ of Cr^{+6} solution. It was observed that maximum regeneration could be achieved within 30 minutes. Then as soon as the Cr^{+6} ions are retrieved, the resin which was reused was again washed with the help of distilled water and then again allowed to mix with the Cr^{+6} concentrations. Different cycles of adsorption and then desorption were followed by keeping the same optimum conditions. During the time of resin regeneration followed by different cycles, the bed depth is always kept as constant. During the proceedings of resin regeneration through different cycles, there was a slight decrease in the breakthrough curve time. The resin regeneration being conducted provides 89.36 % for Cr^{+6} . Similar experiments were conducted repeatedly for four cycles which is presented in Figure 6.5. There was no significant changes in regeneration observed after first cycle.

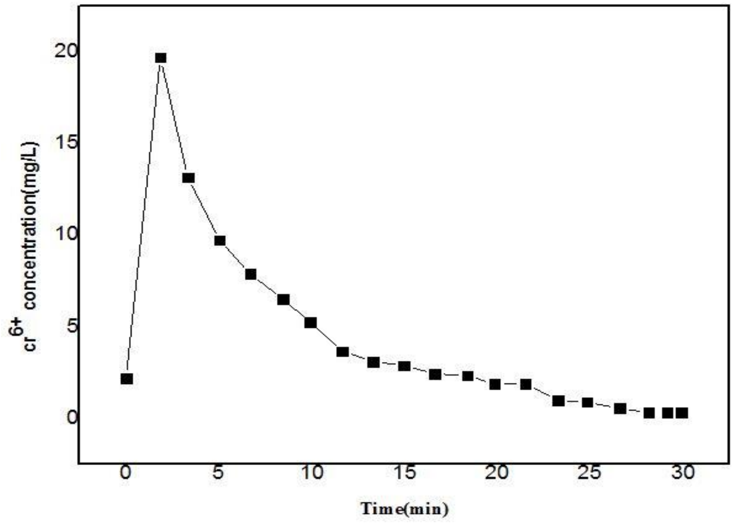


Figure 6.4 Plot of Regeneration

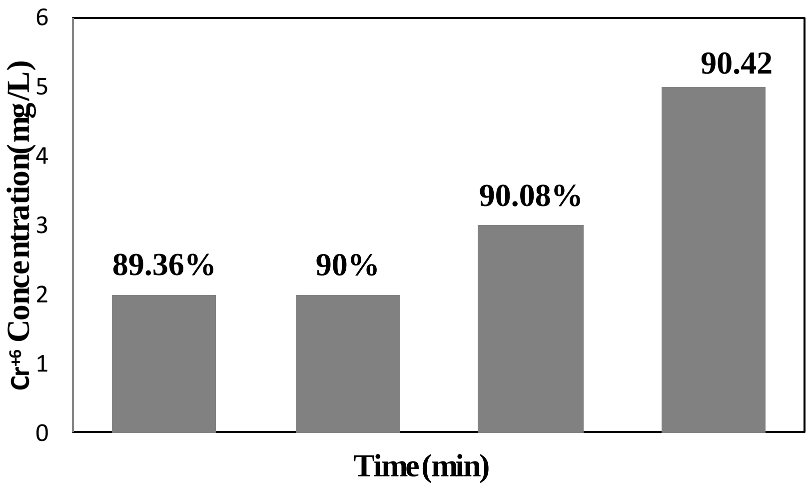


Figure 6.5 Regeneration at different Cr^{+6} concentrations

Table: 6.1: Parameters from column studies

Bed Height (Cm)	**C_o (mg/L)**	**Q (mL/min)**	**Q_{total} (mg)**	**m_{total}**	**Total removal %**	**Q_{eq} (mg/g)**	**C_{eq} (mg/L)**
2	20	3	1.41	2.1	67.14%	0.486	16.571
4	20	3	1.92	2.76	69.56%	0.331	11.23
6	20	3	2.10	2.94	71.42%	0.241	11.21
2	20	3	1.41	2.1	67.14%	0.486	16.571
2	20	5	1.97	3.5	56%	0.848	5.942
2	20	7	2.11	4.9	43.06%	0.727	11.38
2	5	3	0.49	0.52	94.23%	0.168	1.285
2	10	3	0.86	1.05	81.90%	0.296	1.80
2	15	3	1.14	1.575	72.38%	0.393	4.14
2	20	3	1.41	2.1	67.14%	0.486	16.571

6.3 MODELING OF BREAKTHROUGH CURVE

6.3.1 THOMAS MODEL

The plots between ln (C_o/C_t-1) and time in (min) was used to calculate the constants known as k_{th} and q_o as per the Figure 6.6 and Table 6.2 represents the values of these constants. With the increase in the Cr^{+6} concentration and rate of flow, there is a decrease in the constants values of q_o , K_{TH} . Similarly Figure 6.7 shows the plot between ln (Co/Ct-1) and time (min) at varying flow rate. It can be observed from the Table 6.2 that if the depth of the bed increases then the corresponding constant value q_o also tends to increase while K_{TH} tends to decrease .The maximum value of R^2 is found with the low flow rate and maximum height of the column bed. [**95**]

Table 6.2: Parameters using Thomas Model

Conc (mg/L)	Bed height (cm)	Flow rate (mL/min)	K_{th}	q_o	R^2
5	6	3	0.0033	1432.72	0.99
10	6	3	0.00143	3184.63	0.986
15	6	3	0.00083	3680.43	0.97
20	6	3	0.00042	4623.21	0.99
5	2	3	0.00169	3834.07	0.99
5	4	3	0.00074	3784.17	0.98
5	6	3	0.00029	1463.06	0.971

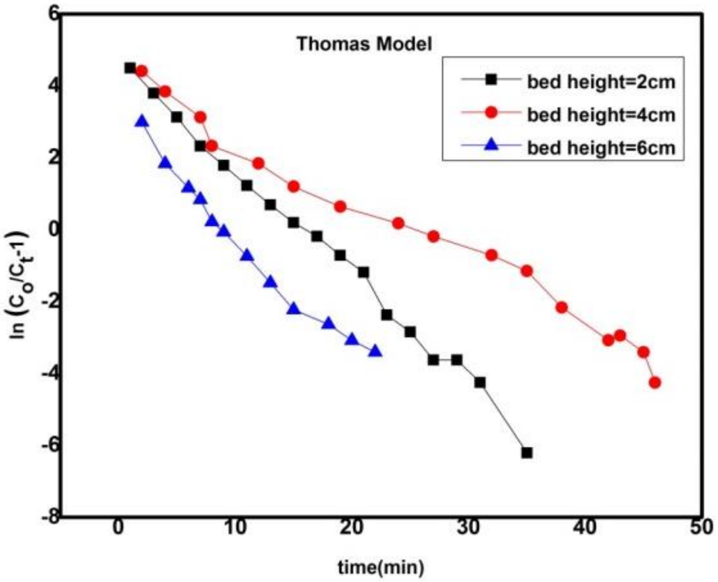


Figure 6.6: Effect of bed height in Thomas model

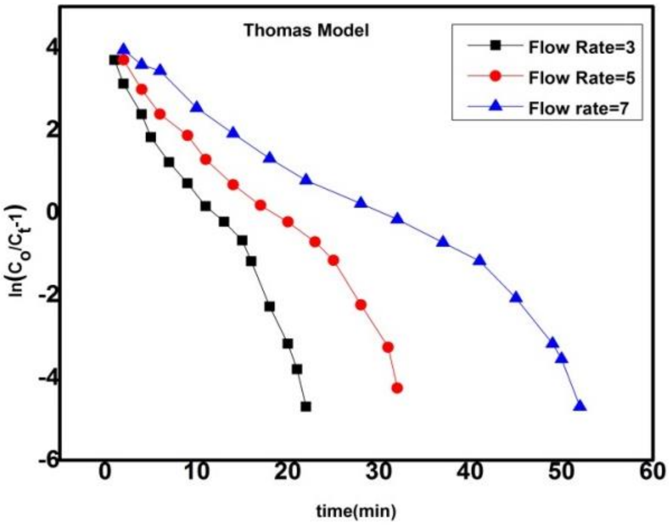


Figure 6.7 Effect of Flow rate in Thomas model

6.3.2 YOON-NELSON MODEL

The plots between ln (C_t/ (C_o-C_t)) and time is used to calculate the constants of the model known as K_{YN} and τ [Figure 6.8 & Figure 6.9].The Table 6.3 represents the respective values of the constants. It is to be noted that the rate constant K_{YN} tends to increase with the increase in Cr^{+6} concentration along with the decreasing trend of achieving 50% of the breakthrough time ,τ. With the increase in bed depth, the value of the breakthrough time, τ tends to increase whereas the constant called as K_{YN} shows a decreasing trend. With the increase in rate of flow, the constants of the model K_{YN} and τ displays an decreasing trend. [**96]**

Table 6.3: Parameters obtained from Yoon Nelson Model

Conc (mg/L)	Bed Height (Cm)	Flow Rate (mL/min)	K_{YN}	T	R^2
5	2	3	0.00647	54.846	0.99
5	4	3	0.00876	43.83	0.97
5	6	3	0.00965	31.49	0.97
5	6	3	0.0160	246.53	0.97
5	6	5	0.018	223.98	0.97
5	6	7	0.021	202.96	0.97

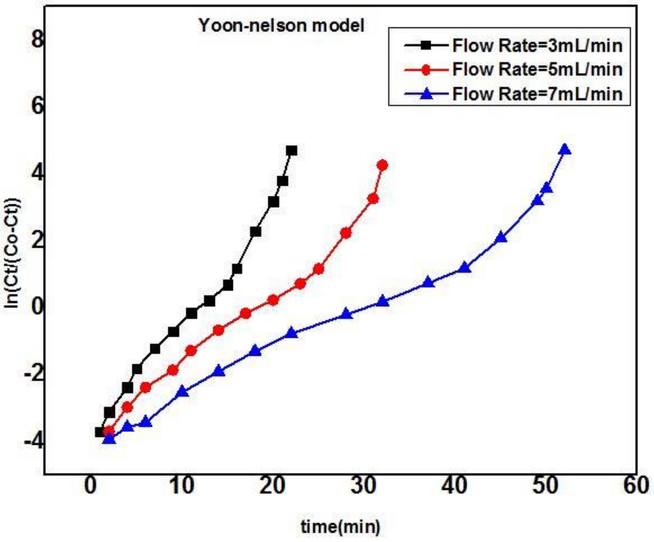


Figure 6.8 Effect of Flow Rate in Yoon-nelson model

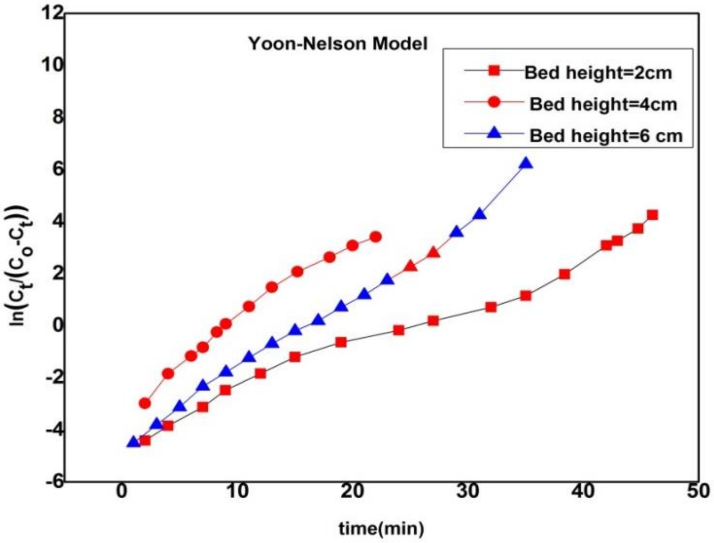


Figure 6.9 Effect of Bed-height in Yoon-nelson model

6.3.3 ADAM- BOHART MODEL

With the increase in Cr^{+6} concentration, the constant of Adam-bohart's model tends to increase whereas with the increase in the rate of flow, it gets decreased as evident from Table 6.4. The values of the constants are estimated from the plots Figure 6.10 & Figure 6.11. Increase in Cr^{+6} concentrations and increase in the rate of flow reduces the respective constant values related to K_{AB} . This demonstrated the occurrence of exchange of mass externally into the interior surface available for adsorption controls the general framework of kinetics present inside the column. In spite of the fact that the Adam-Bohart model proposes a basic and extensive methodology for assessment of adsorption-section test, its legitimacy is constrained to the scope of conditions utilized [**97**]. The coefficient of regression, R^2 lies somewhere around 0.78 and 0.89.

Table 6.4: Parameters obtained from Adam Bohart Model

Conc(mg/L)	Bed Height(Cm)	Flow rate(mL/min)	K_{AB}	N_o	U_o	R^2
5	6	3	0.00537	259.306	0.954	0.78
10	6	3	0.000846	329.63	0.954	0.82
15	6	3	0.000672	440.26	0.954	0.87
20	6	3	0.000423	872.65	0.954	0.89
5	2	3	0.00015	1140.835	0.5979	0.86
5	4	3	0.00037	2190.35	0.3989	0.85
5	6	3	0.00041	3119.04	0.2990	0.74
5	6	3	0.00016	302.98	0.5979	0.89
5	6	5	0.00070	119.20	0.8968	0.89
5	6	7	0.00089	43.219	1.1958	0.84

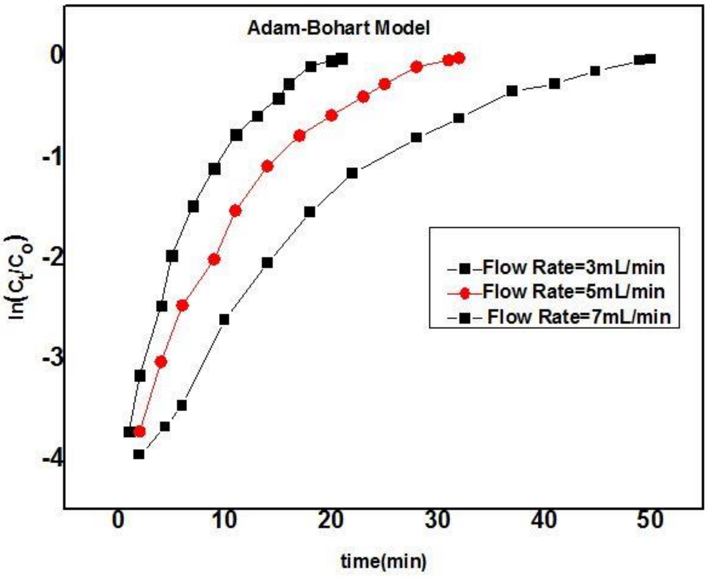


Figure 6.10: Effect of Flow rate in Adam-Bohart Model

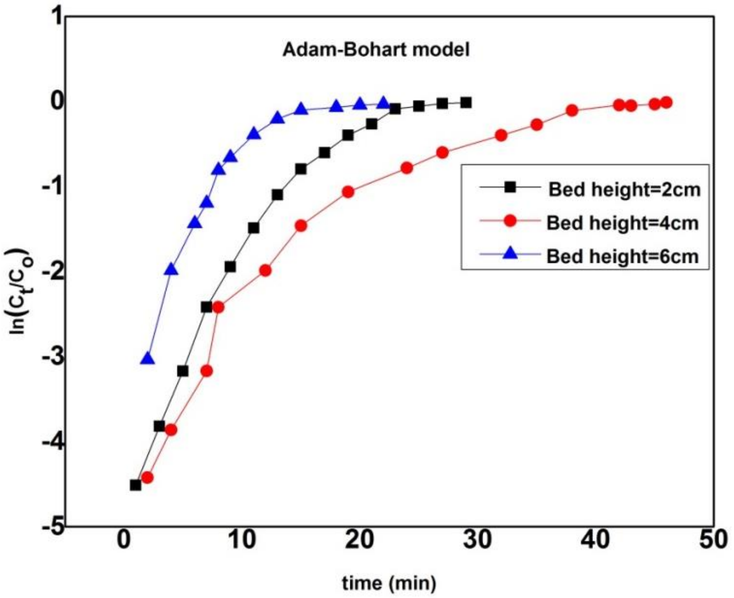


Figure 6.11: Effect of Flow rate in Adam-Bohart Model

Chapter 7

CONCLUSIONS

- Natural resin using cassia gum powder and 4-hydroxybenzoic acid was synthesized at definite process condition.
- Optimum conditions for removal of Cr^{+6} ions (3ppm) using CHBA cation exchange resin at pH of 5-7 , resin amount as 1 g at contact time ~25 min
- The maximum adsorption (99.26%) occurs at 3 ppm of initial concentration using the prepared natural CHBA resin to remediate Cr^{+6} from the drinking water which is generally at low ppm.
- The process of adsorption is followed by second order Pseudo model through the study of kinetics (R^2=0.99). Activation energy was reported as 4.28 KJ/mol. The information obtained from data proves the adequacy towards Freundlich isotherm (R^2-0.99) when the process is said to be in equilibrium and the surface where the adsorption occurs was heterogeneous by nature.
- The hypothetical and analyzed values are closer to each other which prove to be in worthy agreement relating in CHNS analysis.
- FTIR report suggested the addition of N=O group to the prepared resin
- The enthalpy values comes out to be positive which indicates that the process of adsorption is followed by endothermic reaction as well as the entropy values also comes out to be positive shows good binding capacity of Cr^{+6} ions for the resin surface and it also increases the uncertainty of the solid solution interaction during the process of adsorption.
- RSM demonstrated as a helpful system for concentrating on the impact of few components with the variation in their respective response and performing a predetermined number of tests. A second-degree polynomial equation was obtained with the maximum coefficient of regression (R^2) estimation of 99 %.
- Results also showed that the ideal conditions required for Cr^{+6} adsorption were as per the following: amount of resin as (0.43g), at pH (6.13) as well as Initial Concentration of (4.53) with the value of maximum adsorption is 95.05%. The following results were obtained from the box-behenkn design RSM method with a desirability of 0.989.

- The Column performances were evaluated by varying the amount of resin inside the column bed, influent rate of flow with Cr^{+6} concentrations. Furthermore it was seen that with the expansion in height or depth of the bed, the column performance was good or proved to be better.
- The operation of the column is said to be better in lower stream rates at than at higher rates of stream. At low flow rate, the process of adsorption becomes very rapid initially during lower stream rates because of the accessibility for vacant sites of adsorption in such a way that that the presence of Cr^{+6} ions could be captured around the surface of the resin.
- The experimental column data were also expressed in column adsorption models namely Thomson, Yoon-nelson, and Adam-Bohart's model. The data related to the Cr^{+6} adsorption was adequately fitted to the Thomas model with estimated correlated curve as (r^2=0.99).

Scope for Further Research

Various low cost natural adsorbents such as activated charcoal, wheat grain, activated neem leaf powder prepared from activated carbon and groundnut shell powder, Orange Peel, Avena monida (oat), sawdust, rice husk, Papaya wood , maize leaf, modified sawdust of walnut, cocoa shells needs frequent regeneration .All these adsorbents has a major demerit as it requires regeneration, results in loss of adsorbents and is limited to applications for cr^{+6} removal at low pH(<2).

Hence resins have been a good alternative to reduce cr^{+6}.It possess great mechanical properties, good imperviousness to ecological degradation, great glue like properties, low shielding properties ,low shrinkage, easy and quick curing etc. It has been used extensively to treat drinking water due to its important properties such as applicability at neutral pH and capability to treat low concentration of pollutant. The hydrophobic nature can only be seen with the resins which are prepared from divinyl benzene-styrene. Resins which are synthesized mainly from products of petrochemicals, are quite expensive. The two important parameters like the functional groups residing in the resin as well as pH of the respective solution is totally dependent on their capacity of Ion-exchange. Some of the important properties of Ion exchange resins are they are hydrophobic in nature and are non- biodegradable. This is because of the reason of the expansion in the costs of petrochemical items so that Natural man-made materials could be used instead of this ion exchange resins. Tamarind kernel powder, Guar gum Powder, Xanthium gum powder, Sesbania gum powder etc. are extensively used natural products which have been employed for the treatment of waste water by removing several metal ions Such materials are biodegradable as well as are less costly. A few metals holds resins consisting of a series of complexing or chelating lignin's that have been accounted to adequately remove overwhelming metal ions. Thus, due to the increment in contamination level in the water, these types of new materials are employed and this research reports the feasibility of removal of cr+6 ions from water using cassia gum powder resin which is eco-friendly, biodegradable and has high therapeutic property.

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Dissemination

Conferences

1. Shreeparna Mishra and Susmita Mishra, “Preparation and characterization of CHBA resin for removal of Cr^{+6} in drinking water” Conference Proceedings on Sustainable Technology for Cleaner Environment (STCE-2016), N.I.T, Rourkela, Dec 12th -13th, 2015.

Journals (communicated)

1. Shreeparna Mishra and Susmita Mishra, “Preparation and adsorption kinetics of CHBA resin for removal of Cr^{+6} from contaminated water” Journal of Hazardous Materials.(communicated)
2. Shreeparna Mishra and Susmita Mishra, “ Fixed bed column study for Cr^{+6} removal from aqueous solutions using Cassia-4-hydroxy benzoic acid resin” Journal of Environmental Chemical Engineering.(communicated)