KLE Society's
B.V.Bhoomaraddi College of Engineering & Technology
Vidyanagar, Hubli- 580031

Department of Civil Engineering

Research Experience for Undergraduates (REU)

UNDER THE GUIDANCE OF

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CERTIFICATE

Certified that the project work entitled "**USE OF LOCAL SOILS IN ADSORPTION OF CHROMIUM(VI) BY COLUMN STUDY**." carried out by **Miss Supriya Savalkar** , USN **2BV09CV057**, a bonafide student of **BVBCET** in partial fulfilment for the award of **Bachelor of Engineering / Bachelor of Technology** in **Civil Engineering** of the Visvesvaraya Technological University, Belgaum during the year 2012-2013. It is certified that all corrections/suggestions indicated for Internal Assessment have been incorporated in the Report deposited in the departmental library. The project report has been approved as it satisfies the academic requirements in respect of Project work prescribed for the said Degree.

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Signature of Examiners

Name	**Signature and date**
1._____	_____
2._____	_____

USE OF LOCAL SOILS IN ADSORPTION OF CHROMIUM(VI) BY COLUMN STUDY.

ABSTRACT

Polluted water has many pollutants contributing to its state, one of the major being heavy metals like lead, cadmium, chromium etc. This paper focuses on the removal of chromium by adsorption on local soils, since chromium is among the toxic pollutants, since the pollutant on reaching into the human body has proven to be carcinogenic. Chromium is released as waste from mainly tanning, metal finishing industries etc. Chromium exists in different oxidation states and Cr^{+6} being the pre-dominant. The temporary and permanent health hazards include diarrhea, stomach and intestinal bleeding, cramps in liver and in some cases even kidney damage. The different codes and standards define the permissible limits of chromium in drinking water. Since its permissible limits are necessary to assess the degree of pollution and treatment that is to be given. Since the leachate from the waste on transferring on to the landfill must not percolate via the compacted layers and testing of soils for its adsorption capacity becomes a major concern since the water table will be contaminated and therefore urges for a material that is locally available and can be used as filler material in landfills that can withheld the oozing of the contaminant (i.e. better adsorption capacity of the soil) as well as the leachate intercepting the streams during wet season.

The steps to be followed to conduct this observation mainly include study of soil properties, preparation of standard/stock solution and the method of analysis. The method that is adopted for adsorption of Chromium includes Batch test and Column test with the arrival of the results with its reference to the isotherms that are drawn from the experimental results.

The maximum percentage removal of chromium occurs at the adsorbent depth of 30cm and occurs maximum for 4ppm, i.e. 31.25%.

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MOER	Minimal National Standards
WPOOF	Waste Pomace Of Olive Oil Factory
EAM-CCRCB	Ethylamine modified chitosan carbonized rice husk composite beads.
RSM	response surface methodology

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CHAPTER-1

INTRODUCTION

1.1GENERAL

Man has been always dependent on the environment for his very survival extracting benefit from it as well as serving it from time to time thereby maintaining a delicate balance between him and his surroundings. If he strikes the balance he must be ready for the consequences further as the intricacy of various elements is hampered that gradually breaks down as the worst situation. In the course of last few decades man's relation with its environment has changed drastically due to his unreasonable expectation followed by his activities to further imbalance things. The progress in science and technology and its beneficial application in fulfilling the never ending demands of man have left no part of biosphere untouched, thus making his life precarious. The modifications that occur every now and then in the environment has lead to placement of materials from one place to another thereby converting less degradable forms to harmful. The reason that can be quoted is that the population that is increasing and the need to cater its increasing demands. But the capacity of the environment to suffice these increasing demands has to be assessed.

The environment provides man with three basic amenities required for his sustenance. The first being the living space and other amenities to make his life comfortable around. Secondly, the environment which is the source of food, water and other resources and lastly a sink to dump the wastes that is assimilated. Thus the capacity of the environment to perform these functions is to be assessed and care has to be taken so that these are not impaired. It is important to study the stress imposed on the environment, the rate of excessive use of resources and also to note the pollutant intercepting from industries.

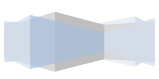
Rapid growth in the population, unplanned cities and towns and growth and expansion of industries and industrial areas are the common features of our country. Whereas rise in slum dwellers, pollution be it air, noise, soil or any type in that matter of fact is at its peak. The soil contamination, the pollution of rivers and subsoil waters due to use of fertilizers and pesticides in farms and the same due mishandling in the natural water bodies is abrupt and thereon increasing.

Depending upon the purpose of the industry the waste water consists of different pollutants. Chromium finds varied range of application in the industries and the different materials manufactured thereon.

Few applications of chromium:

- Magnetic tape that forms the part of audio cassettes is made from the chromium
- Chromium (III) oxide is a metal polish.
- It is used in preparation of chromic acid that is used to clean the laboratory glass wares.
- Leather tanning is done by Chromium (III).
- It is used in preparation of dyes.
- It is used as a preservative.
- Chromium is added to iron in the manufacture of stainless steel.
- The alloys prepared from adding chromium are good temperature resilient and can be used in turbines, jet engines etc.
- Chromium is hard and corrosion resistant and can be used for metal coating.

Discharge of the wastes to the water bodies poses a serious problem to the receiving water as well as its consumers that is the biodiversity that exits there. Since it is well known fact that chromium is carcinogenic and adversely affects the digestive tract.



1.2NEED FOR THE STUDY

The very purpose of this research is justified with its experimental application in the field of Solid Waste Management, thus it becomes necessary to briefly know the content of this waste. A few questions like: - What is Solid Waste? How is it generated? What is its composition? How should it be disposed? What is its relevance with respect to the statement of research? Is it a grey area with respect to results or findings or there exists a well-defined prospectus. The next set of questions like how suitable is the material of interest, what procedure is apt for its accurate determination of chromium, chemicals required and above all the properties of soil. Now let us answer these questions one by one.

Solid waste or simply waste is nothing but unwanted useless debris that creates nuisance when not managed properly. These wastes are generated from households, commercial centres, industries and institutions of a locality. Thus solid waste can be defined as combined waste that is generated from the above places. Its composition can be broadly classified into biodegradable and non-biodegradable. This includes wastes like organic material, paper, glass, plastic, metal etc...These wastes are to be disposed of properly so as to avoid pollution. There are many methods of disposing these wastes by recycling, incineration and if not by these methods going in for landfill as the last resort. For this filler materials generally called as liner materials are used, the property of this material directly influences the behavior against the percolation of the waste water or the leachate into the ground water. The liner materials are classified into clayey, plastic and composite liner material. The geo-membranes also find wide application in the liner material. The landfill in engineering terms is a well gauged depression or the dump yard where in the waste entry is closely monitored. The used of this liner material is for both the bottom lining and the top cover.

In the course of time answering the question as why chromium becomes necessary. Chromium is a heavy metal and being carcinogenic it becomes more important to assess its content in waste water because when this waste water joins streams or ground water causes serious pollution thus questioning its basis of usage. Chromium is 24th abundant element in the

earth's crust and has wide application in metal finishing, tanning etc and since these small scale industries do not have enough capital to set up a waste treatment plant the waste joins the municipal waste line and is treated at the treatment plant. It becomes necessary to assess the composition of waste and conduct umpteen tests to derive at the final result. Many researches are conducted on low cost easily and locally available material. The basic concept in this research is the adsorption capacity the locally available soil i.e. Halumannu. The soil properties are determined and for its application in the landfill as the liner material. The property of concern will be permeability of the soil i.e. Low permeability. Once these properties are determined next is the laboratory procedure to determine the adsorption capacity of the material.

Image 1.1 Top view of the landfill

Image 1.2 Dumpyard.

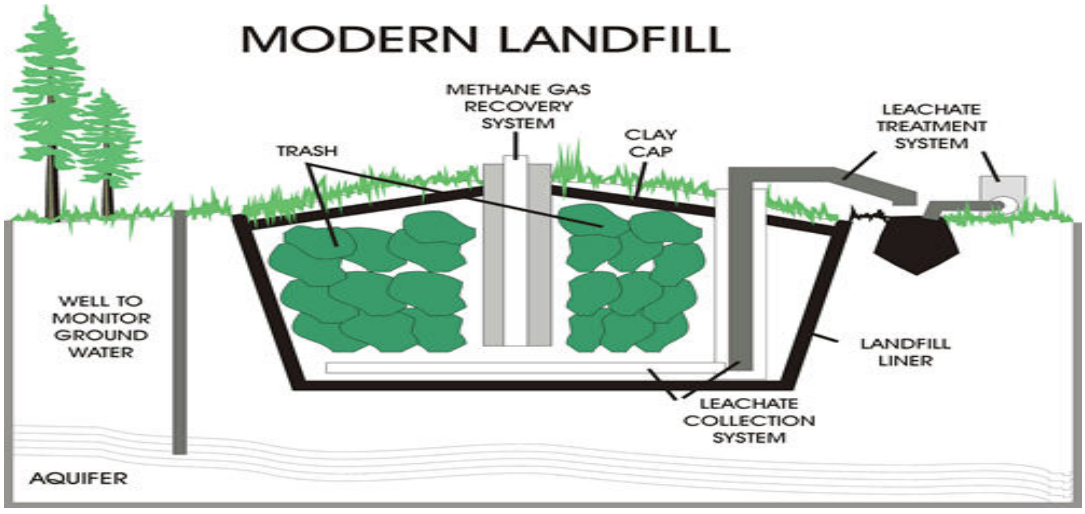
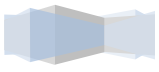


Image 1.3 Cross-section of landfill

CHAPTER-2

STUDY OF ADSORPTION



2.1THEORY OF ADSOPRTION

Adsorption is the process by which ions or molecules present in one phase tends to condense and concentrate on the surface on the surface of another phase. The material that adheres is called adsorbate and the adsorbing material is termed as adsorbent. Adsorption is a surface based process involving the volume of the material. It is the result of surface energy exerted by the material itself. There are three types of adsorption.

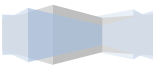
- Physical
- Chemical
- Exchange adsorption

Physical adsorption is due to the existence of Vander Waals forces between molecules. The adsorbed material may condense and form several superimposed layers on the surface of adsorbent.

Chemical adsorption is as the result of stronger than that in physical adsorption and lead to the formation of chemical compounds. This forms a monolayer on the adsorbent and is not free to move.

Exchange adsorption is due to adsorption electrical attraction between the adsorbate and the surface.

Example: The mechanism in water purification using activated charcoal.



2.2MECHANISM

There exist charges on the surface of the adsorbent as well as adsorbate that is responsible for the adsorption property. There exits unbalanced forces on the surface that are decreased due to the process of adsorption. Due to this the surface energy decreases considerably and this is accompanied by evolution of heat.

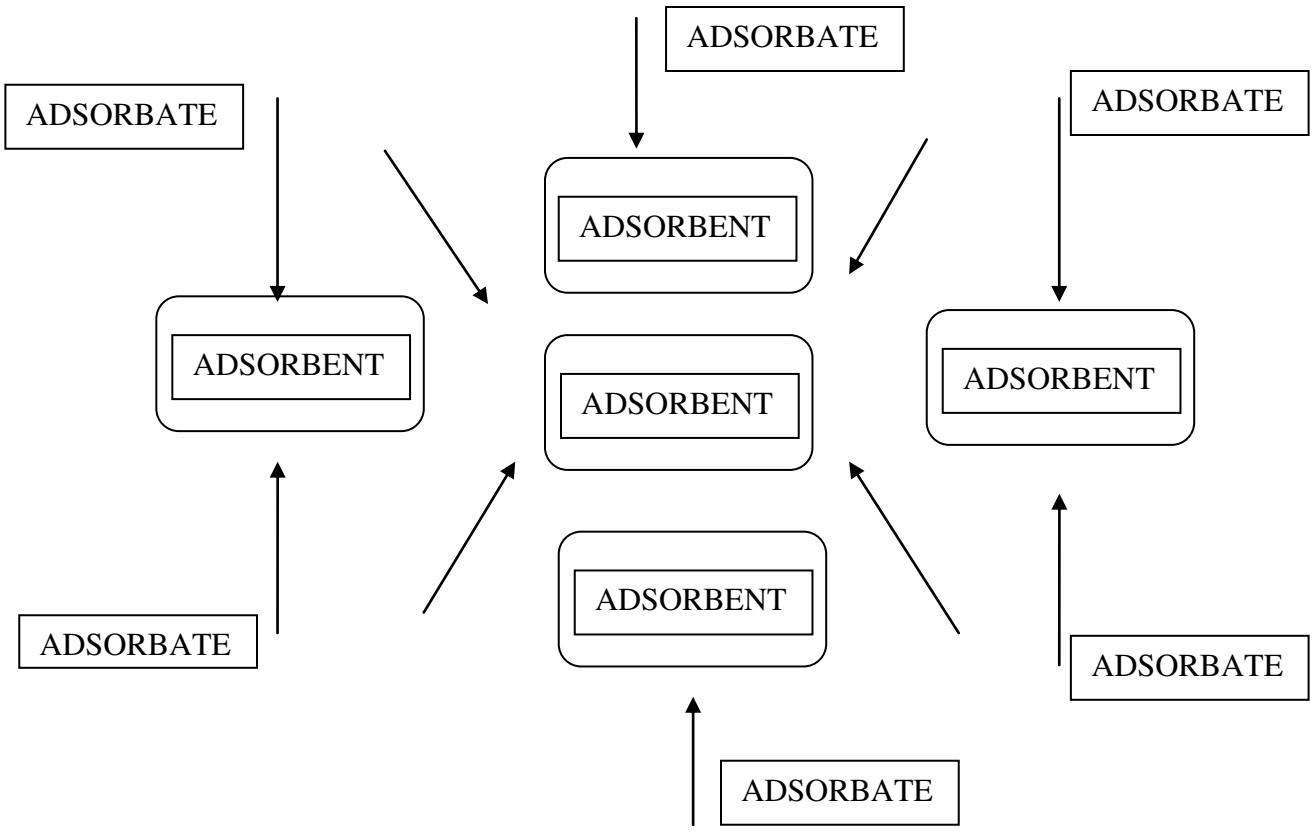


CHART 2.1: Figure showing adsorption mechanism

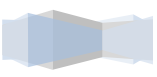
2.3 PROPERTIES OF ADSORBENT

- It must have large specific area.
- The pore must be small.
- The bulk density must be high.
- It should not be toxic.
- It should be cheap.
- Ease of availability.

2.4 FACTORS INFLUENCING ADSORPTION

- The adsorption process is due to the attraction of adsorbate molecules over the adsorbent forces due to the residual forces. Thus the specific nature of the adsorbate and the adsorbent are necessary to access the degree of adsorption.
- The surface area of the adsorbent is the prime reason for greater adsorption power. This force of attraction increases on increasing the surface area and also the residual forces on subdivision.
- Since it is exothermic reaction the experimental conditions define the effect on the adsorption process.

  Example: Adsorption decreases with increase in the temperature. The other parameters like pressure, time, pH etc also have pronounced effect on the process.



2.5 APPLICATIONS

The adsorption process finds its application in vivid areas in science. A few of them are:

- The fuller earth is used in refining of petroleum and oils. It finds its application in decolorizing of sugar solution with activated charcoal, wherein the color is eliminated.
- The softening of hard water by zeolite process.
- The catalytic action of the catalyst is due to adsorption of reactants on its surface.
- The action of drugs is due to their adherence on the microbes and later killing them.
- The dyeing with the help of dyes is based on the principles of adsorption.
- In glass masks wherein suitable adsorbents are used so that the poisonous gases present in the atmosphere are adsorbed and the air is purified.
- In preserving vacuum
- In paint industry since the paint should not contain dissolved gases as the spreading and adhering property will be hampered. Thus suitable adsorbents are used to remove these dissolved gases.
- In chromatographic studies.

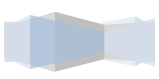
2.6 ANALYSIS OF ADSORPTION.

The adsorption process is a three stepped process defined by the three steps viz:

- Macro transport -involves the movement of adsorbate through liquid phase to the liquid solid interface by advertion and diffusion.

- Micro transport – this involves the diffusion of the adsorbate material through the macro pore system to the adsorption sites in the micro pore and sub micro pores.

- Sorption- it is the attachment of the adsorbate material to the adsorbent. It is difficult to bifurcate between chemical and physical adsorption thus sorption comes into picture.



Equilibrium is said to be achieved when the rate of sorption equals the rate of desorption and the adsorbent capacity has been reached. The adsorption isotherm gives the idea of the theoretical adsorption capacity.

The basis for this is that the quantity of adsorbate that can be taken up by an adsorbent is function of both the features and concentration of the adsorbate and the other parameters like temperature, pH etc. The amount of material adsorbed is determined as a function of the concentration at constant temperature, this function thus obtained is termed as adsorption isotherm. These experimental results were defined by Freundlich, Langmuir and BET. The Langmuir isotherm aligns more with the experimental data as compared to the others. The Freundlich isotherm is the special case of Langmuir isotherm.

2.6.1FREUNDLICH ISOTHERMS

The empirical formula derived for this is,

$$(x/m)=K_F\ (C_e)^{\wedge\ (1/n)}$$

Putting the above equation in logarithmic form.

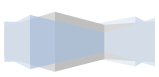
$$\log(x/m) = \log K_F + (1/n)\log (C_e)$$

Where **(x/m)** - Amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

C_e- Equilibrium concentration of adsorbate in solution after adsorption (mg/l)

K_F and **n** are empirical constants representing the adsorption capacity and intensity of adsorption respectively.

The constants in Freundlich's isotherm can be determined by plotting **log(x/m)** v/s **log (C_e).** From the intercept and slope, the values of K_F and **(1/ n)** were calculated respectively.



2.6.2LANGMUIR ISOTHERMS

This is derived from the rational consideration, Langmuir isotherm is defined as

$$(x/m) = (K_L\, b\, C_e) / (1+b\, C_e)$$

The above equation can also be written as

$$C_e/(x/m) = (1/b\, m)\, [(1/ K_L) + C_e]$$

Where **(x/m) -** Amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

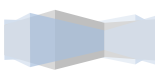
C_e- Equilibrium concentration of adsorbate in solution after adsorption (mg/l)

K_F and **n** are empirical constants and can be determined by plotting **$C_e/(x/m)$** v/s **(C_e).**

The Freundlich and Langmuir isotherms are appropriate and can be tested only when the corresponding plots are straight lines. But in practice the plots obtained are often found to be a reasonably straight line.

CHAPTER-3

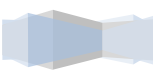
LITERATURE SURVEY



3.1 STUDIES ON ADSORPTION OF CHROMIUM (VI)

Many groundwater resources in the world have been contaminated by solid and liquid wastes containing chromium (VI) generated by electroplating, leather tanning and wood preservative industries. Cr (VI) is highly toxic, highly soluble in water, and may be transported over long distances in the subsurface. This transport depends upon geo-hydrological conditions and geo-chemical processes. The contaminated groundwater is usually treated either by chemical reduction followed by precipitation or by biological processes. The first alternative involves large quantities of chemicals and the precipitate formed needs further attention. On the other hand, biological treatment offers an environment friendly and economical alternative.

Many tests are conducted for the behavior analysis of hexavalent chromium and to know the effect it has on the environment. Cr (VI) is toxic to humans and is found in water. It has been shown toxic when in aerosol form causing damage to the skin and upper respiratory system and causing lung cancer and it is a suspected carcinogen. The maximum permissible limit of Cr (VI) for discharge into inland surface water is 0.1 mg/L and in portable water is 0.05 mg/L. The Ministry of Environment and Forest Government of India has set minimal national standards of 0.1 mg/L for safe discharge of effluent containing Cr (VI) in surface water. The tests conducted to know the removal of chromium is done either by Batch Test or Column Study and later the chromatographic analysis. [1]



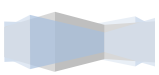
3.2 COLUMN STUDY

The biological treatment of groundwater can be carried out either ex situ or in situ. Ex situ method involves costly pumping operation. In situ method involves either the enhancement of native Cr (VI) reducing bacteria. In this work, bench-scale column experiments were conducted to evaluate the effectiveness of Cr (VI) containment by bio-remediation processes in aquifers. Effects of (i) ground water velocity, (ii) initial microbial concentration and (iii) aquifer soil characteristics on Cr (VI) containment were studied.

Soils used in this study were collected from the I.I.T. Madras campus, Chennai, India. They were surface soils collected from the unsaturated zone. Soils thus collected were sieved; the portions which passed through 4.75mm were sterilized, cooled to room temperature and preserved in clean plastic containers for subsequent use. For sand column experiments, river sand, which passed through 0.6mm and retained in 0.425mm sieves was washed thoroughly with distilled water and oven dried at 100 ◦C over night.

It was one m long and had a square cross section (10 cm×10 cm). An overhead tank with provision for an adjustable head served as the inlet to the column. A porous plate was provided at the inlet in order to achieve a uniform entry of water into the soil. A collection reservoir was provided at the outlet. Water level in the outlet reservoir was maintained above the top of the soil column in order to maintain saturated conditions in the column. Sampling ports were provided on the sides at four different cross sections at distances 20, 40, 60 and 80 cm from the inlet, respectively.

The prepared sterilized soil was filled in the column in 33 layers of approximately 3 cm thickness. The column was compacted in vertical direction. Each layer was compacted with 25 blows of a 1.2 kg hammer falling from a 30 cm height, in order to get a more or less uniform compaction. The dry weight of the soil was measured before adding the required moisture and filling the column. This information was used to determine the bulk density of the soil. Constant heads were maintained in the head and tail tanks for 6–24 h (6 h for soil B and 24 h for soil A) to obtain a steady flow rate through the soil column. The flow rate was monitored with respect to time by collecting the water at the outlet. [2]



The potential use of the brown seaweed, Ecklonia, biomass as a bioreductant for reducing Cr(VI) was examined in a continuous packed bed column. The effects of the operating parameters, such as influent Cr(VI) concentration, influent pH, biomass concentration, flow rate and temperature, on the Cr(VI) reduction were investigated. Increases in the influent Cr(VI) concentration and flow rate or a decrease in the biomass concentration inside the column led to a higher breakthrough of the Cr(VI) ions in the effluent. Particularly, the influent pH and temperature most significantly affected on the breakthrough curve of Cr(VI); a decrease in the influent pH or an increase in the temperature enhanced the Cr(VI) reduction in the column. For process application, a non-parametric model using neural network was used to predict the breakthrough curves of the column. Finally, the potential of the column packed with Ecklonia biomass for Cr(VI) detoxification was demonstrated.

Biosorption, using biological materials, has known as an alternative process for the removal of heavy metals from aqueous. solutions, as this novel approach is effective and cheap Because of these advantages, there has been extensive research exploring appropriate biosorbents that are able to effectively remove Cr(VI) Continuous reactor used in this study consists of a 53 cm long and 3 cm internal diameter glass column, i.e., total volume of it is 375 mL. The column was densely packed with a known amount (52.5 or 26.3 g) of dried biomass. The process was operated in an up-flow mode, and set at constant temperature with the aid of a water bath.

The effluent Cr(VI) concentration was below 0.1 mg L−1 for the first 15 beds, and then sigmoidlly increased to 79.4 mg L−1 by the 274th beds. The total Cr concentration rapidly increased in the effluent, finally reached that of the influent level. The difference between the total Cr and Cr(VI) concentrations indicated that the Cr(VI) was reduced to Cr(III) by contact with the biomass packed inside the column. [3]

The fixed-bed columns were made of Perspex tubes 2.0 cm internal diameter and 30 cm in height. The bed length used in the experiments was 10 cm. In a typical experiment the metal of a known concentration was pumped at a fixed flow rate to the filled with known bed height of adsorbent. The particle size of adsorbent used in the experiment was 1.0–3.0 mm. The pH of the solutions was maintained constant at 2.0. The temperature of stream feeding solution and of the column was controlled at 25 ◦C through a thermostatic bath. The bed porosity was 0.20.
The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The breakthrough curves show the loading behavior of metal to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed metal concentration (C_{ad} = inlet metal concentration (C_0) −outlet metal concentration (C_t)) or normalized concentration defined as the ratio of effluent metal concentration to inlet metal concentration (C_t/C_0) as a function of time or volume of effluent for a given bed height. In the sorption of chromium (VI) to WPOOF, a change in inlet chromium (VI) concentration affected the operating characteristics of the fixed bed column. The sorption breakthrough curves obtained by changing inlet chromium(VI) concentration from 50 to 200 mg L^{-1} at 10mLmin^{-1} flow rate and 10 cm bed height. At the highest metal concentration (200 mg L^{-1}) the WPOOF bed saturated quickly leading to earlier breakthrough and exhaustion time. Tested different initial Cr (VI) concentration, maximum bed capacities at 50, 75, 100 and 200 mg L^{-1} Cr (VI) concentration were 0.98, 1.06, 1.17 and 1.47 mg g^{-1}, respectively. The driving force for adsorption is the concentration difference between the Cr (VI) ion on the adsorbent and the metal ion in the solution. During the feed solution was sent to the column, upwards of 50% of the inlet Cr6+ concentration was exhausted in the initial times. The 50 mg L^{-1} of Cr^{6+} solutions was exhausted within 360 min (114.6 BV), the 75 mg L^{-1} Cr^{6+} solutions was exhausted within 300 min (95.54 BV), 100 mg L^{-1} Cr^{6+} solutions was exhausted within 180 min (57.3 BV) and 200 mg L^{-1} Cr^{6+} solutions was exhausted within 120 min (38.2 BV) respectively. The more metal ion concentration was higher, the more adsorbent usage rate was increased and the adsorbent exhaustion rate was higher value. While adsorbent exhaustion rate was 6.53 g L^{-1} at 50 mg L^{-1} Cr6+ ion concentration, adsorbent exhaustion rate obtained at 19.58 at 200 mg L^{-1} Cr^{6+} ion concentration. [4].

The objective of this present study is the optimization of process parameters in adsorption of Cr(VI) ions by ethylamine modified chitosan carbonized rice husk composite beads (EAM-CCRCBs) using response surface methodology (RSM) and continuous adsorption studies of Cr(VI) ions by ethylamine modified chitosan carbonized rice husk composite beads (EAM-CCRCBs). The effect of process variables such as initial metal ion concentration, adsorbent dosage and pH were optimized using RSM in order to ensure high adsorption capacity at low adsorbent dosage and high initial metal ion concentration of Cr(VI) in batch process. The optimum condition suggested by the model for the process variable such as adsorbent dosage, pH and initial metal ion concentration was 0.14 g, 300 mg/L and pH2 with maximum removal of 99.8% and adsorption capacity of 52.7 mg/g respectively. Continuous adsorption studies were conducted under optimized initial metal ion concentration and pH for the removal of Cr (VI) ions using EAM-CCRCBs. The breakthrough curve analysis was determined using the experimental data obtained from the continuous adsorption. Continuous adsorption modeling such as bed depth service model and Thomson model were established by fitting it with experimental data. [5]

The removal of chromium ions from aqueous waste solution using Ca-alginate (CA) beads, immobilized alive and dead Cunninghamella elegans beads was investigated in batch and fixed bed column. In batch studies the behavior of the adsorption was investigated through studding the influences of contact time, pH, initial Cr (VI) concentration, immobilized fungal biomass (IFB) load and temperature. The Cr (VI) removal rate increased with a decrease in pH and increase in initial Cr (VI) concentration. The maximum removal of Cr (IV) achieved at pH 2.0. The immobilized fungal biomass increased the Ca-alginate sorption capacity by at least two fold. Equilibrium and kinetic analyses were done to estimate sorption capacities, rates and the possible reaction mechanisms. Langmuir and Freundlich isotherms were used to fit the equilibrium isotherm. The desorption of Cr (IV) using dist. H2O was found to be efficient than other alkaline solutions, because it maintain the viability and mechanical strength of the different beads throughout five repeated cycles with little decrease in its removal capacities. Column experiments were also done to evaluate the continuous removal of chromium ions by the different beads. The effect of; bed heights (4.5, 9.0, 13.5 cm), feed flow rates (1, 2, 3ml/min) and inlet chromium ions concentrations (25, 50, 100 ppm) on the breakthrough curve were studied using immobilized dead Cunninghamella elegans (Cun. el.) beads. According to the sorption

capacity, the immobilized dead Cun. el. beads can be considered as a suitable biosorbent for applications.[6]

The adsorption of Cr (VI) onto waste acorn of Quercus ithaburensis was studied using fixed-bed adsorption. The experiments were conducted to study the effect of important design parameters such as flow rate, solution pH and particle size of adsorbent. Decrease in adsorbent particle size and flow rate produced a better bed capacity. Also an increase in flow rate and particle size resulted in a decrease in the bed volumes at the breakthrough. The highest bed capacities of fixed-bed column were obtained at pH 2.0. The present investigation aimed the heavy metal sorption from synthetic wastewaters with another pollutant matter. For this reason, the Cr(VI) removal from aqueous solutions through waste acorn of Quercus ithaburensis may be evaluated as an environmentally friendly and extra economic treatment. These studies show that waste acorn is an effective and inexpensive adsorbent for chromium (VI) removal from aqueous solutions. In fixed-bed column, the adsorption capacity is strongly dependent on the flow rate, pH of solution and particle size. The bed volumes slightly increased as flow rate and particle size was decreased. As the flow rate increased, the breakthrough curve became steeper, the break point time and adsorbed ion concentration decreased. With an increase in influent pH, the bed volumes treated decreased. In addition, the bed volumes slightly increased as flow rate and particle size were decreased. Thomas and Yoon–Nelson model were used in analysis of column performance data and the model parameters were evaluated. [7]

The breakthrough curves of Cr (VI) on bagasse fly ash (BFA) at room temperature were measured in a fixed-bed apparatus. It has been tried to fit the experimental data to fixed-bed model for breakthrough curve. Then the effective diffusivity of hexavalent chrome ion was obtained. The effective diffusivity can be used to predict breakthrough curves at other adsorption conditions. The fly ash adsorption will be low cost method, which may be economically affordable to be applied in small and medium scale industries. Breakthrough curve has been obtained by the continuous adsorption experiment using two different columns filled by fly ash as the adsorbent. The bed porosity of the both column is similar at 0.44. The first column has a 42 cm of height of the bed and contain of 65 g of fly ash. The second column height is 21.5cm and packed with 10 grams of fly ash. Cr (VI) solution flows continuously upward the column at

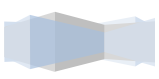
velocity of 0.1 cm/s. the adsorption breakthrough curves of ion Cr (VI) carrying in the first column. The breakthrough time is in a range of 20 to 50. [8]

In the column study, the experiments were conducted in a glass column with 2 cm internal diameter and 50 cm height under down flow mode. For determination of the flow rate effect, three columns were used. Each column was packed with 3.4 g of adsorbent with a particle size of 0.4 mm to reach a bed height of 10 cm. The initial Cr (VI) concentration of 100 mg/l at pH 2 was pumped through the packet columns by a peristaltic pump. The effluent flow rate was adjusted for each column according to 5, 10 and 15 L/min. The effluent solution was collected at regular interval time for determination of Cr (VI). Similarly, the effect of the initial influent concentrations of Cr(VI) was investigated in the same conditions but the flow rate was kept constant (5mL/min) and varied concentration ranging from 50, 100 and 150 mg/L. To obtain data of the bed depth service time (BDST), the experiments were carried out with three columns that were packed with 3.4, 6.8 and 10.8 g of adsorbent giving the bed depths of 10, 20 and 30 cm, respectively. The influent solution with concentration of Cr (VI) of 100 mg/L at pH 2 was passed through columns at flow rate 5ml/min. The concentration of Cr (VI) in the effluent was determined by method which was mentioned above. [9]

Biosorption of heavy metals is emerging as an effective technology for the treatment of industrial wastewater. In this study, biosorption potential of Padina boergesenli–a brown marine alga was assessed in the removal of Cr (VI) from electroplating effluent. In order to yield different bed heights, 22, 26 and 30 g of biomass were added to produce 30, 35 and 40 cm height, respectively. The sorption breakthrough curves obtained by varying the bed heights from 30 to 40 cm at 10 mL/min flow rate and 100 mg/L initial chromium concentration for P. boergesenli biomass .The chromium uptake capacity of the biomass was 13.2, 13.5 and 13.7 mg/g for 30, 35 and 40 cm of bed heights, respectively. Flow rate on chromium biosorption by P. boergesenli was studied by varying the flow rate from 3 to 10 mL/min, while the bed height and initial chromium concentration were held constant at 30 cm and 100 mg/L, respectively The flow rate also strongly influenced the chromium uptake capacity of P. boergesenli as 33.4, 28.0, 19.1 and 13.2 mg/g, which were recorded at 3, 5, 7 and 10 mL/min, respectively.[10]

CHAPTER-4

MATERIALS AND METHODOLOGY



4.1GENERAL

To study the percentage of chromium that is adsorbed on the surface of the adsorbent and thereby removed. The adsorbent for the study is the locally available soil called Halumannu. This is achieved by the column test experiments. The material of prime concern is the adsorbent, the locally available soil, Halumannu .the soil has to be sieved through a sieve of 75 micron and the soil passing and retained on the pan has to be taken for all the experimental purposes. The soil has to be packed in a air-tight container.

4.2MATERIALS AND APPARATUS

Column test

- Stock solution of chromium
- Diphenyl carbazide solution
- Distilled water
- Adsorbent(Halumannu)
- Column of 2cm diameter
- Whatmann Filter Paper No1
- Glass wool
- 250ml capacity conical flask
- Sulphuric acid
- Spectrophotometer

a. STOCK SOLUTION OF CHROMIUM

The chromium stock solution is prepared by dissolving 2.83g of L.R grade $K_2 Cr_2 O_7$ in 1000ml of distilled water. This is got from the standard s preparation manual. To get the solution of known concentration the stock solution is diluted.

Image 4.1 $K_2 Cr_2 O_7$ (L R grade) crystals.

Image 4.2 Chromium Stock Solution

- Chromium (Cr)-derived from Greek word Chroma meaning colour.
- Atomic number-24, is a transition metal belonging to Group6, Period4 and block ‘d.
- It is steely gray, lustrous, hard metal that takes high polish and has a high melting point. It is odorless, tasteless and malleable.
- It is 24th abundant element in earth’s crust and is found in a concentration of 100ppm.
- Chromium exists in different oxidation states ranging from +6 to -2.
- It has body centered cubic crystal structure.

b. DIPHENYL CARBAZIDE SOLUTION

the diphenyl carbazide solution is used as a colorimetric reagent that is prepared by dissolving 250mg of 1,5, Diphenyl carbazide in 50ml of acetone (LR grade).this is stored in some dark colored bottle when the color fades the solution is discarded.[11]

Image 4.3 Diphenyl carbazide solution

Image4.4 1,5, Diphenyl carbazide

c. ADSORBENT(HALUMANNU)

Halumannu is name of the locally available soil. The sieved through a sieve of 75micron and the soil retained on the pan is taken for experimental purpose.

Image 4.5 HALUMANNU

SOIL PROPERTIES

SOIL PROPERTY	OBSERVED VALUE
Natural moisture content	3.5%
Atterberg limits	
Liquid limit	51%
Plastic limit	39.80%
Shrinkage limit	22.70%
Plasticity index	11.20%
Grain size analysis	
Gravel	15.80%
Sand	38.10%
Silt	30.10%
Clay	15.8%
Specific gravity	2.3
OMC	19.40%
MDD	1.74g/cc
Permeability	$1.80*10^{-7}$ m/s

Table No 4.1 Soil Properties

d. WHATMANN FILTER PAPER NO1

The solution is filtered through the Whatmann Filter Paper No, to get a clear solution that is further tested for the change in concentration by checking its absorbance using a spectrophotometer at a wavelength of 540nm.

Image 4.6 Whatmann Filter Paper No1

e. GLASS WOOL

Since in column study there is downward flow of the chromium solution passing through bed of the adsorbent there is every chance of the adsorbent flowing out of the column thus the Glass wool is used to plug the bottom

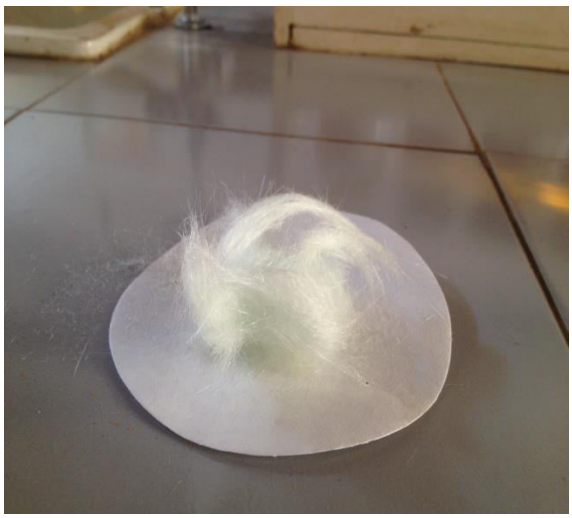


Image 4.7 Glass wool

f. COLUMN OF 2CM DIAMETER

For column test a glass column of 2cm is taken. The end opening is plugged by glass wool so that the soil does not pass along with the chromium solution. The soil bed size is varied from 2cm to40cm.

Image 4.8 Column

The column procured is 2cm in diameter and 50cm in length. It is a knob operated column and its opening is plugged with glass wool so that the adsorbent does not flow down along with the chromium solution. The column is washed with distilled water and dried.

g. SPECTROPHOTOMETER

Image 4.9 spectrophotometer

Image 4.10 spectrophotometer showing quivets

The spectrophotometer used for experimental purpose is a UV double beam spectrophotometer. It is a LAB INDIA make; named UV LAB INDIA 3000+.the wavelength set for the study purpose is 540nm.the solution used for calibration is distilled water treated as blank.

4.3PROCEDURE

4.3.1COLUMN TEST

- The stock solution is prepared as mentioned in (a) and it is diluted with distilled water to get lower concentrations.
- Firstly the calibration curve is plotted with concentrations of chromium solution ranging from 1ppm to 10ppm.
- The adsorbent is fixed in the column in bed sizes ranging from 2cm to 40cm.
- The parameters to be considered include concentration, pH and bed size.
- 100ml of chromium solution is passed through the adsorbent fixed in the column set up. This solution has a downward flow and is collected in a conical flask through which the solution running down is filtered.
- The filtrate (97ml) is taken in a conical flask and to this add 2-3drops of sulphuric acid and 2ml of 1, 5 diphenyl carbazide solution, wine red color appears. The 1, 5 diphenyl carbazide solution is a coloring reagent which helps is absorbance of light of 540nm wavelength. The pH maintained is 7.
- Calibrate the spectrophotometer (UV Lab India 3000+) with the blank solution of distilled water in a quivet and set it to a wavelength of 540nm.
- In another quivet take the colored solution and read the absorbance in the spectrophotometer.
- The concentration of this solution is obtained by interpolating the values obtained from the calibration curve,
- The percentage removal of chromium is calculated from the relation

  Percentage removal = (change in concentration/initial concentration)*100

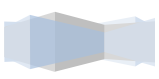
- The results are to be plotted for the isotherms.

Image 4.11 filtrate after developing colour

Image 4.12 filtrate for column study

CHAPTER-5

RESULTS



5.1 RESULTS OF COLUMN STUDY

CONCENTRATON(ppm)	ABSORBANCE
BLANK	
0	0.0000
1	0.1500
2	0.2700
3	0.3600
4	0.4200
5	0.5000
6	0.5500
7	0.6000
8	0.6200
9	0.6500
10	0.6800

Table No 5.1 Calibration Curve

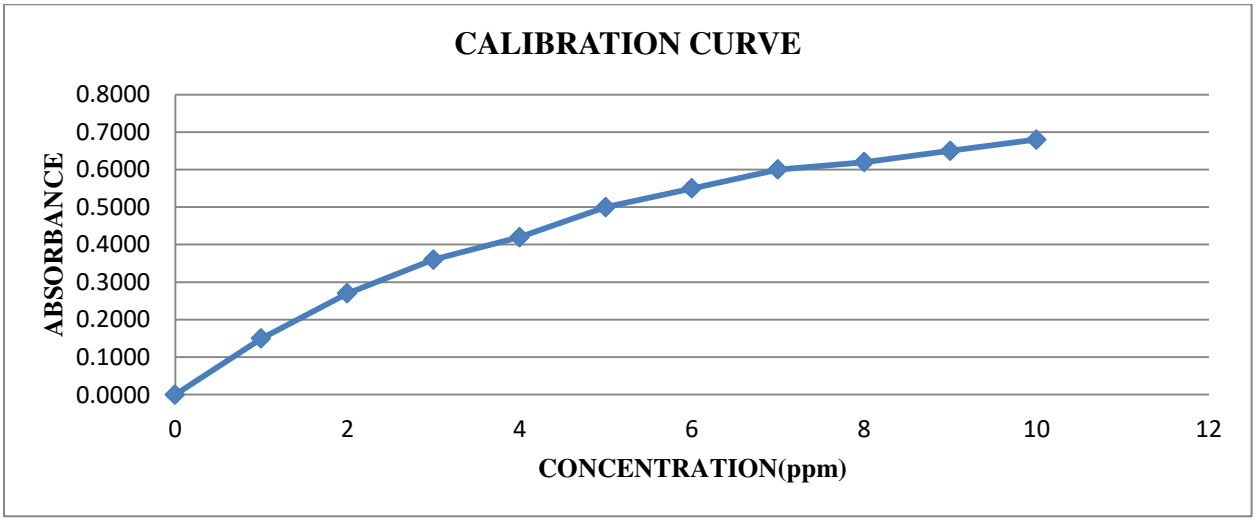


CHART 5.1: Calibration Curve, Plot of Concentration V/S Absorbance

BED SIZE=2cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.90	5.00
4	3.92	2.00
6	5.85	2.50
8	7.80	2.50
10	9.75	2.50

Table No 5.2 Percentage removal for a bed size of 2cm

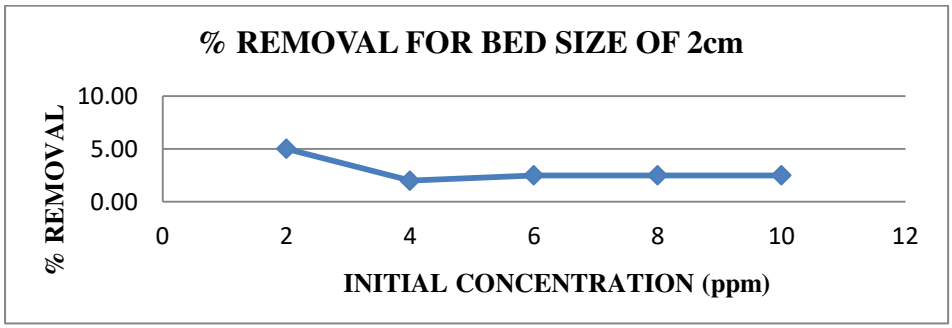


CHART 5.2 Plot of initial concentration (ppm) v/s %removal for bed size of 2cm

BED SIZE=4cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.80	10.00
4	3.80	5.00
6	5.74	4.33
8	7.70	3.75
10	9.67	3.30

Table No 5.3 Percentage removal for a bed size of 4cm

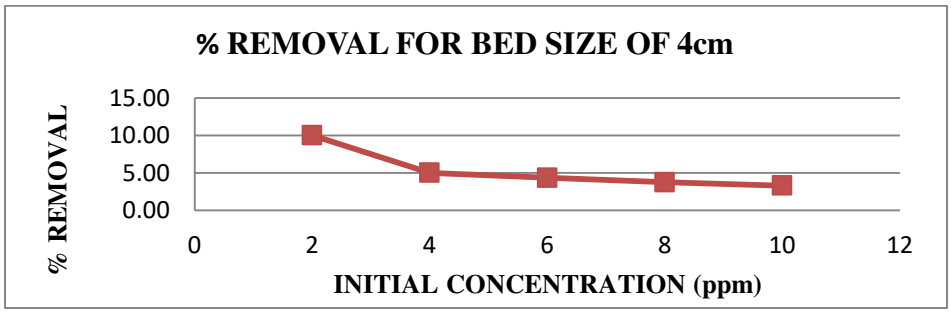


CHART 5.3 Plot of initial concentration (ppm) v/s %removal for bed size of 4cm

BED SIZE=6cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.70	15.00
4	3.75	6.25
6	5.60	6.67
8	7.55	5.63
10	9.50	5.00

Table No 5.4 Percentage removal for a bed size of 6cm

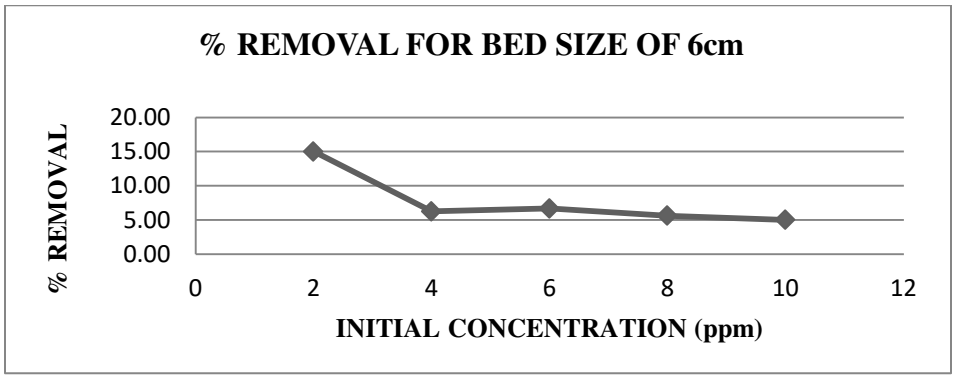


CHART 5.4 Plot of initial concentration (ppm) v/s %removal for bed size of 6cm

BED SIZE=8cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.65	17.50
4	3.60	10.00
6	5.45	9.17
8	7.30	8.75
10	9.20	8.00

Table No 5.5 Percentage removal for a bed size of 8cm

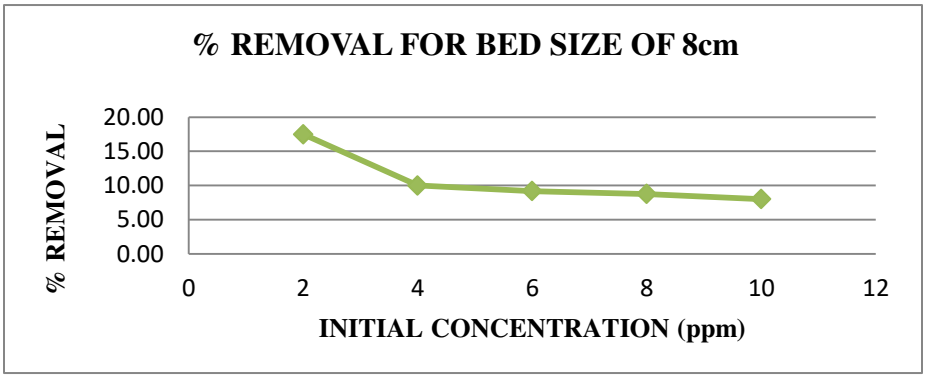


CHART 5.5 Plot of initial concentration (ppm) v/s %removal for bed size of 8cm

BED SIZE=10cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.58	21.00
4	3.45	13.75
6	5.30	11.67
8	7.15	10.63
10	8.95	10.50

Table No 5.6 Percentage removal for a bed size of 10cm

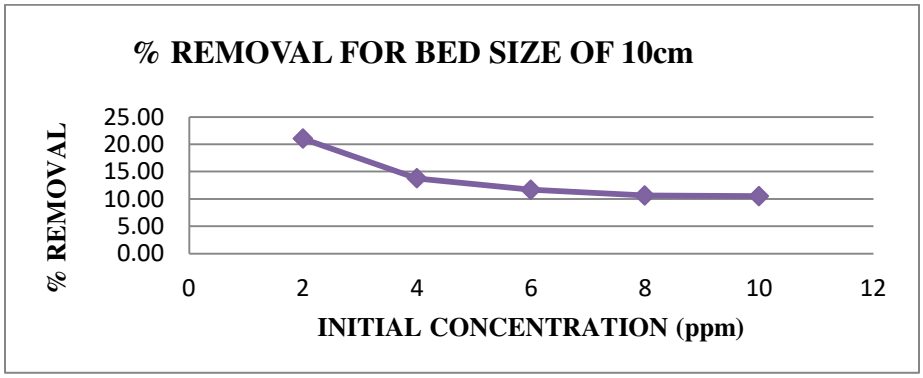


CHART 5.6 Plot of initial concentration (ppm) v/s %removal for bed size of 10cm

BED SIZE=12cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.50	25.00
4	3.30	17.50
6	5.20	13.33
8	7.00	12.50
10	8.80	12.00

Table No 5.7 Percentage removal for a bed size of 12cm

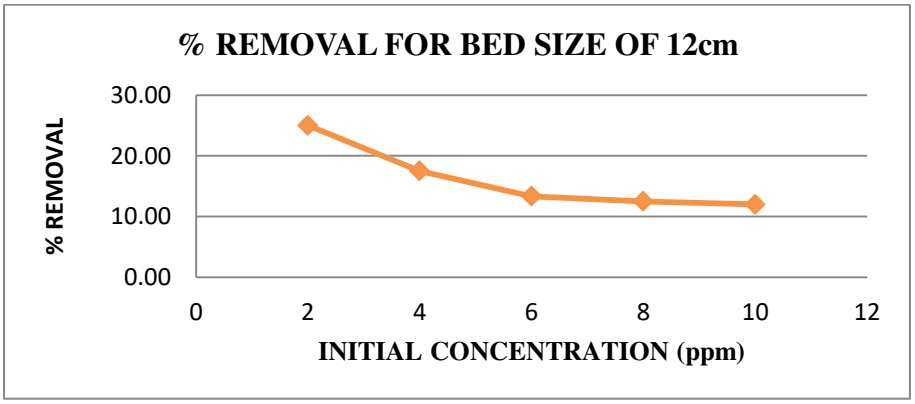


CHART 5.7 Plot of initial concentration (ppm) v/s %removal for bed size of 12cm

BED SIZE=15cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.48	26.00
4	3.20	20.00
6	5.00	16.67
8	6.80	15.00
10	8.60	14.00

Table No 5.8 Percentage removal for a bed size of 15cm

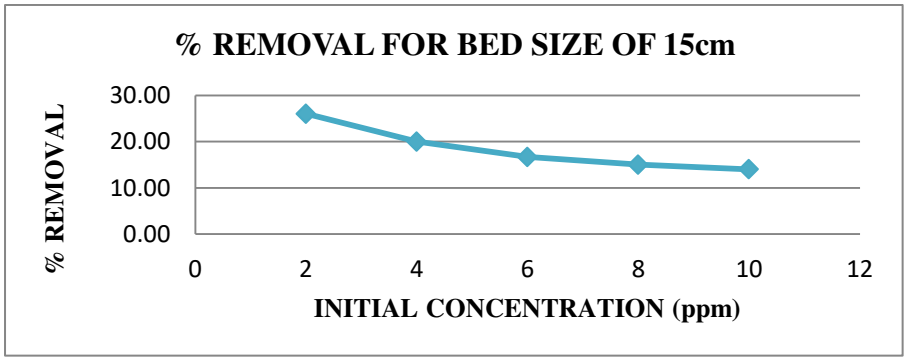


CHART 5.8 Plot of initial concentration (ppm) v/s %removal for bed size of 15cm

BED SIZE=20cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.46	27.00
4	3.00	25.00
6	4.85	19.17
8	6.50	18.75
10	8.40	16.00

Table No 5.9 Percentage removal for a bed size of 20cm

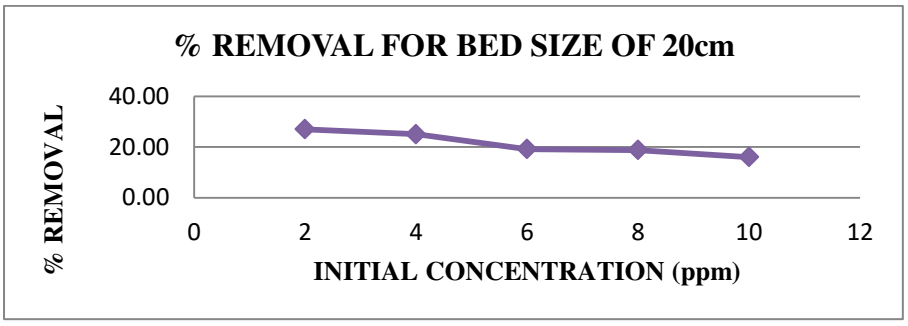


CHART 5.9 Plot of initial concentration (ppm) v/s %removal for bed size of 20cm

BED SIZE=25cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.44	28.00
4	2.85	28.75
6	4.60	23.33
8	6.35	20.63
10	8.20	18.00

Table No 5.10 Percentage removal for a bed size of 25cm

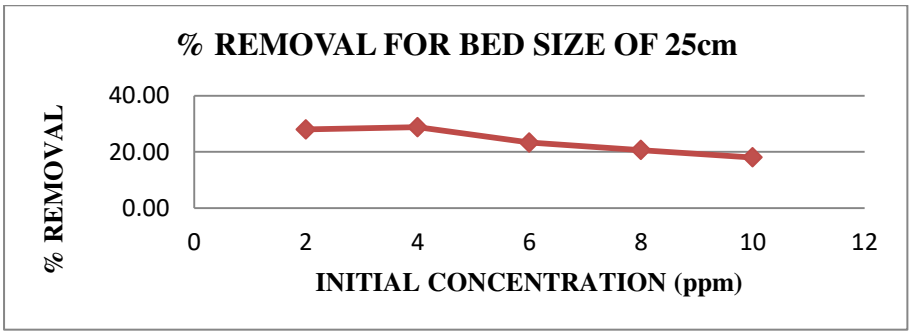


CHART 5.10 Plot of initial concentration (ppm) v/s %removal for bed size of 25cm

BED SIZE=30cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.44	28.00
4	2.75	31.25
6	4.50	25.00
8	6.30	21.25
10	7.90	21.00

Table No 5.11 Percentage removal for a bed size of 30cm

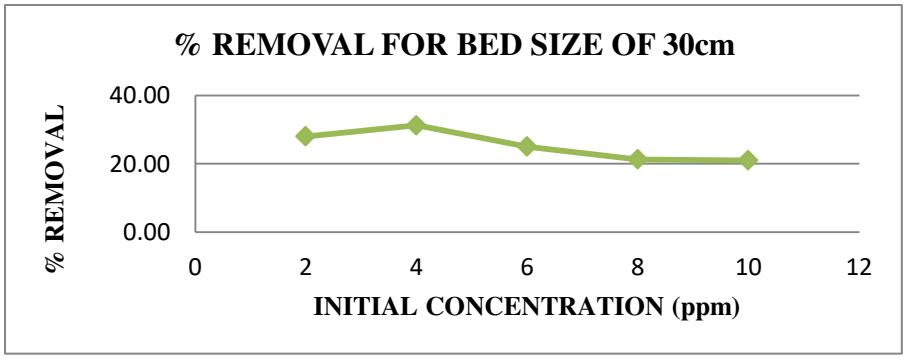


CHART 5.11 Plot of initial concentration (ppm) v/s %removal for bed size of 30cm

BED SIZE=40cm

INITIAL CONCENTRATION (ppm)	FINAL CONCENTRATION (ppm)	% REMOVAL
2	1.436	28.20
4	2.75	31.25
6	4.49	25.17
8	6.20	22.50
10	7.86	21.40

Table No 5.12 Percentage removal for a bed size of 40cm

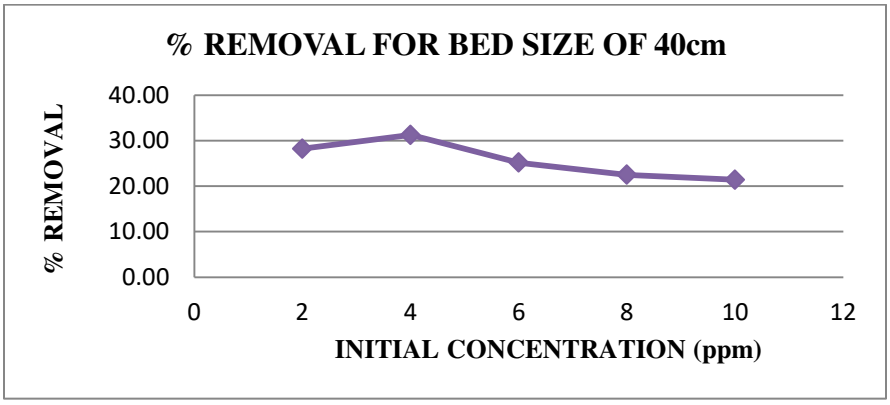


CHART 5.12 Plot of initial concentration (ppm) v/s %removal for bed size of 40cm

BEDSIZE(cm)	% REMOVAL FOR 2ppm	% REMOVAL FOR 4ppm	% REMOVAL FOR 6ppm	% REMOVAL FOR 8ppm	% REMOVAL FOR 10ppm
2	5.00	2.00	2.50	2.50	2.50
4	10.00	5.00	4.30	3.75	3.30
6	15.00	6.25	6.67	5.63	5.00
8	20.00	10.00	9.17	8.75	8.00
10	22.50	13.75	11.67	10.63	10.50
12	25.00	17.50	13.33	12.50	12.00
15	26.00	20.00	16.67	15.00	14.00
20	27.00	25.00	19.17	18.75	16.00
25	27.40	28.75	23.33	20.63	18.00
30	**28.00**	**31.25**	**25.00**	**21.25**	**21.00**
40	28.20	31.25	25.17	22.20	21.40

Table No 5.13 Optimum bed size for various concentrations

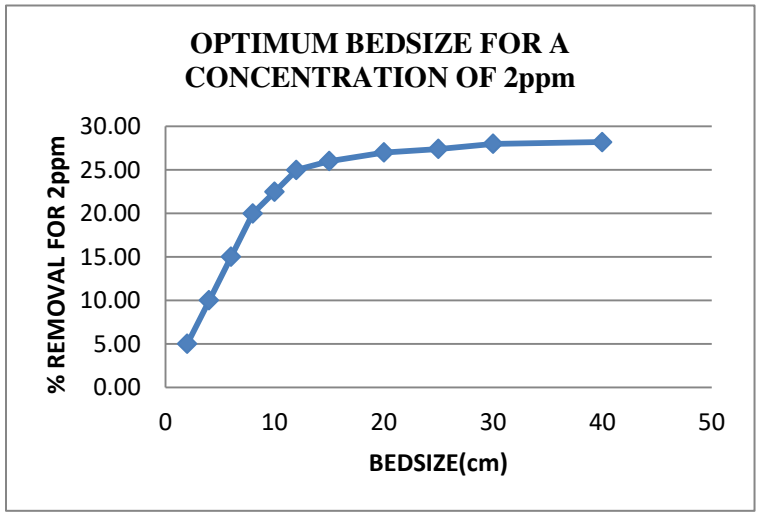


CHART 5.13 Optimum bed size for 2ppm

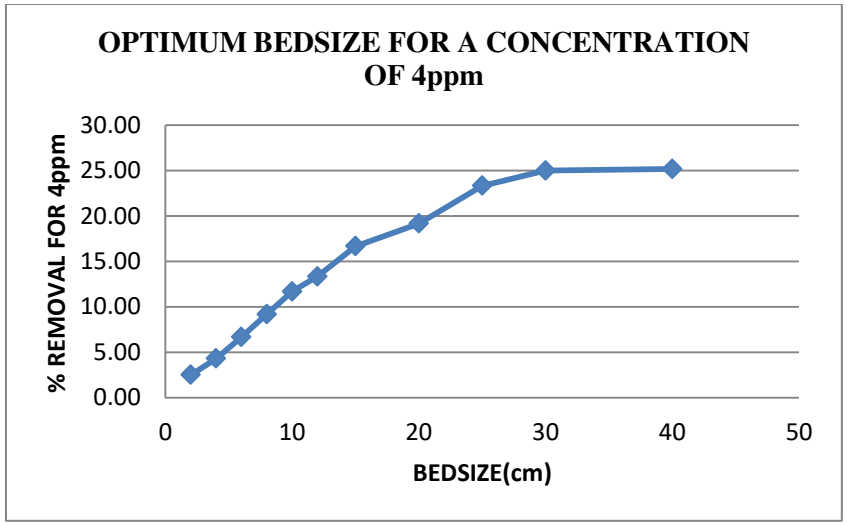


CHART 5.14 Optimum bed size for 4ppm

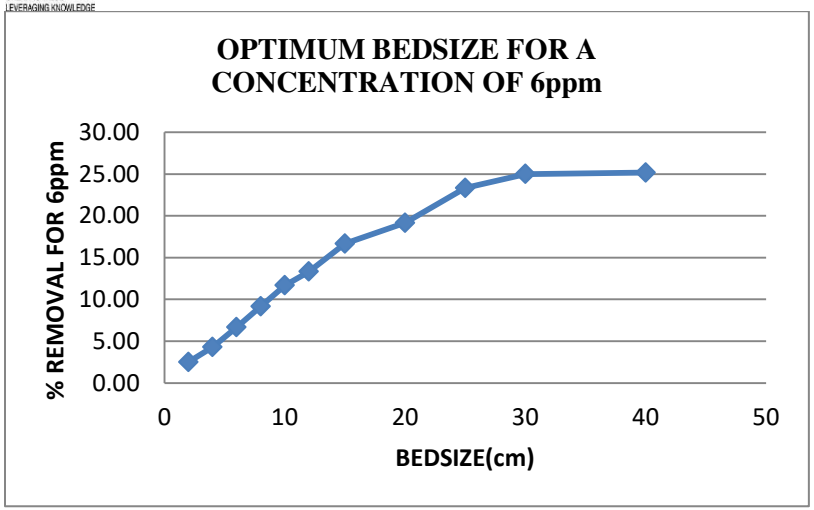


CHART 5.15 Optimum bed size for 6ppm

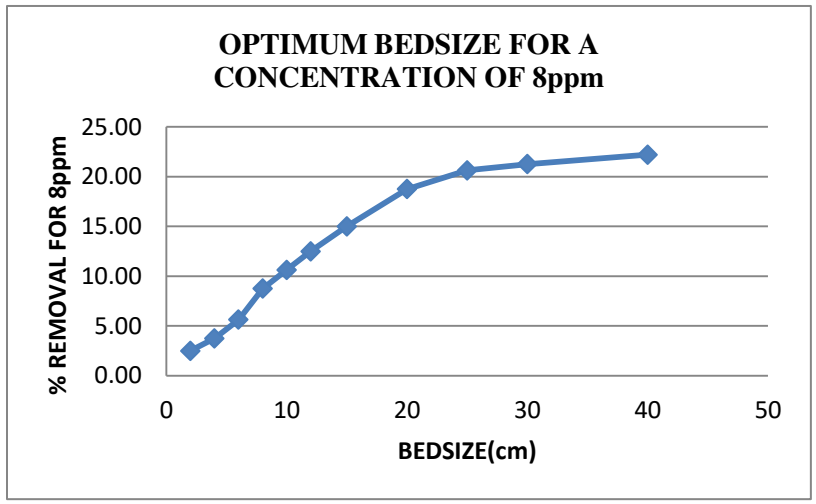


CHART 5.16 Optimum bed size for 8ppm

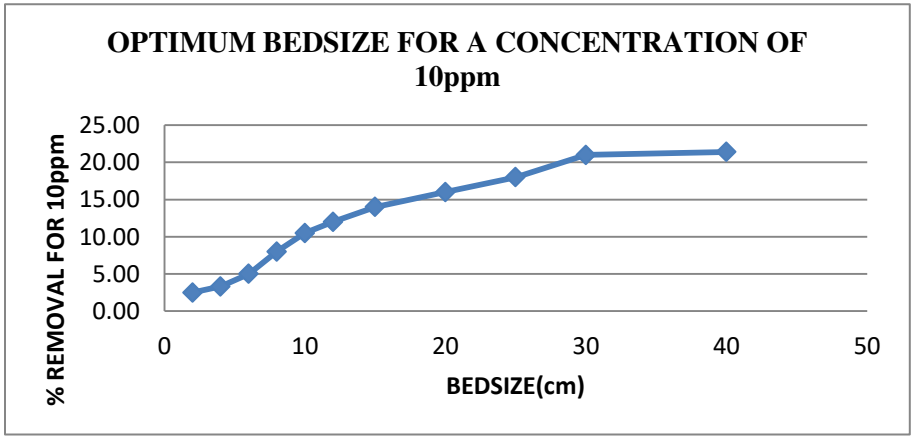


CHART 5.17 Optimum bed size for 10ppm

5.2COMMENTS

It is seen from the results that the adsorption value goes on increasing with the depth of the adsorbent bed size upto a depth of 30cm and thereon is nearly constant. The depth of the adsorbent bed is varied from a minimum of 2cm to a maximum of 40cm. the column is of 2cm diameter and 50cm height. The bottom of the column is plugged with glass wool to prevent the down flow of the adsorbent with the solution. The soil is packed in the column and is lightly compacted in layers of 2cm each. The solution flows through the column and the rate of flow is maintained with the help of knob. The maximum percentage removal of chromium occurs at the adsorbent depth of 30cm and occurs maximum for 4ppm, i.e. 31.25%. It is seen from the plots that the percentage removal of chromium goes on decreasing for a constant bed size. The valves of the final concentration of the solution are studied from the results obtained from the spectrophotometric analysis. The values of final concentration are obtained from the calibration curve where it is computed from the absorbance values. The percentage removal of chromium is obtained by

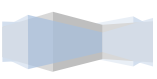
$$\frac{\mathbf{Ci - Cf}}{\mathbf{Ci}} * \mathbf{100}$$

Ci-Initial concentration in ppm

Cf- Final concentration in ppm

CHAPTER-6

CONCLUSION



6.1 OVERVIEW

The whole idea behind conducting the experimental tests on adsorption properties of the locally available soil, i.e. Halumannu is to check its feasibility as a liner material. The tests conducted on this include the batch study and column test. The colorimetric analysis procedure gives the insight of the adsorption characteristics of the soil. Since it is known fact that the clay is considered to be a good liner material since its permeability is less. The adsorbent is also tested for its geotechnical properties to address its suitability.

SOIL	PERMEABILITY ,K cm/s	RELATIVE PERMEABILITY
Coarse gravel	Exceeds 10^{-1}	High
Sand, clean	10^{-1} to 10^{-3}	Medium
Sand, dirty	10^{-3} to 10^{-5}	Low
Silt	**10^{-5} to 10^{-7}**	**Very low**
clay	Less than 10^{-7}	impervious

Table no 6.1 The permeability range of different soil categories

Since this soil falls in the very low relative permeability zone it can be used as a liner along with the provision for incorporating some membrane. Column test results are to be used to simulate the adsorption capacity of the soil.

6.2PARAMETERS

6.2.1 EFFECT OF CONCENTRATION

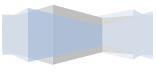
Since it is known from the standards that the permissible limit for chromium for discharge into inland surface water is 0.1 mg/L and in portable water is 0.05 mg/L, the adsorption of the same goes on decreasing for a constant pH, but reaches a saturation point. It is seen that the solution with lower has maximum percentage removal of chromium as compared with the higher concentration. Since the surface area goes on increasing with the increase in the depth of the bed the resulting into higher percentage removal in comparison to the initial solution as per the standards the permissible limit is very low for that of chromium at such low levels the efficiency in removal is higher. Thus the Halumannu can be said to be a good adsorbent.

6.2.3EFFECT OF BESDSIZE

The percentage removal of chromium goes increasing upto a certain point before attaining saturation. In case of column test the maximum removal is obtained at a concentration of 4ppm for the bed sixe of 30cm. Further the value reaches a saturation point and remains more or less constant. It is seen that the percentage removal goes on increasing with the depth of the bed size for a constant concentration. For all the varying concentrations it is seen from the results that the maximum removal of chromium is obtained at a depth of 30cm. thus this depth of the bed can be considered optimum for further change in the variables and can be checked for the same.

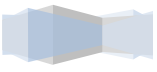
6.3FUTURE SCOPE

- The test has to conducted for other variables like change in pH, rate of flow, checking the percentage removal from the setup at different levels, temperature etc.
- To validate the results isotherms are to be plotted (in progress).
- Trying out combination of some soil of lower permeability and repeating the steps to check their composite action.



CHAPTER-7

REFERENCES



[1] Tarun Kumar Naiyal, Biswajit Singha and Sudip Kumar Das. 'FTIR Study for the Cr(VI) Removal from Aqueous Solution Using Rice Waste'. 2011 International Conference on Chemistry and Chemical Process
IPCBEE vol.10 (2011)

[2] [1] T. Shashidhar, Ligy Philip, S. Murty Bhallamudi. 'Bench-scale column experiments to study the containment of Cr(VI) in confined aquifers by bio-transformation'. Journal of Hazardous Materials B131 (2006) 200–209)

[3] Donghee Park , Yeoung-Sang Yun , Dae Sung Lee ,Seong-Rin Lim, Jong Moon Park 'Column study on Cr(VI)-reduction using the brown seaweed Ecklonia biomass'. Journal of Hazardous Materials B137 (2006) 1377–1384)

[4] Emine Malkoc , Yasar Nuhoglu, Murat Dundar, 'Adsorption of chromium(VI) on pomace—An olive oil industry waste:Batch and column studies' Journal of Hazardous Materials B138 (2006) 142–151)

[5] S. Sugashini and K. M. Meera Sheriffa Begum 'Column Adsorption Studies for the Removal of Cr(VI) Ions by Ethylamine Modified Chitosan Carbonized Rice Husk Composite Beads with Modelling and Optimization' Journal of Chemistry Volume 2013 (2013), Article ID 460971.

[6] Abdel-Razek A.S. ' Removal of chromium ions from liquid waste solutions using immobilized Cunninghamella elegans' . Nature and Science 2011; 9(7):211-219]. (ISSN: 15450740)

[7] Emine Malkoc , Yasar Nuhoglu , Y¨uksel Abali ;' Cr(VI) adsorption by waste acorn of Quercus ithaburensis in fixed beds: Prediction of breakthrough curves' Chemical Engineering Journal 119 (2006) 61–68

[8] Chandra W. Purnomo, and Agus Prasetya,' The Study of Adsorption Breakthrough Curves of Cr(VI) on Bagasse Fly Ash (BFA)' Proceedings of the World Congress on Engineering and Computer Science 2007 WCECS 2007, October 24-26, 2007, San Francisco, USAISBN:978-988-98671-6-4

[9] Nguyen Van Suc, Tran Nguyen Khanh Hung.' BATCH AND COLUMN STUDIES FOR ADSORPTION OF Cr (VI) FROM AQUEOUS SOLUTION BY COIR PITH OF NIPA PALM FRUIT (NYPA FRUTICANS)', EJEAFChe, 11 (3), 2012. [238-252]

[10] E Thirunavukkarasu and K Palanivelu,' Biosorption of Cr(VI) from plating effluent using marine algal mass' Indian Journal of Biotechnology Vol 6, July 2007, pp 359-364

[11] Determination of hexavalent chromium in waters by a colorimetric method-Laboratory Methods Manual