EXPERIMENTAL STUDIES ON REMOVAL OF POLLUTANTS BY ADSORPTION

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Abstract

Wastewater treatment has increasingly become a critical focus in recent years due to the escalation in the levels of toxins present in industrial effluents. Of particular concern are the high concentrations of toxic heavy metals like chromium (VI) found in aqueous streams, stemming from the release of untreated effluents containing metals into water sources, posing a significant environmental challenge. Adsorption stands out as an efficient technique for eliminating chromium (VI) from wastewater. The exploration of biosorbents has emerged as a key area of interest for removing chromium (VI) ions from aqueous solutions at ambient temperature.

In this study, raw tamarind fruit shells after being activated through treatment with concentrated hydrochloric acid (98% w/w) was used as an adsorbent. Equilibrium studies showed that adsorption of chromium (VI) is more effective at lower solution pH values.

Packed beds are known for their ability to remove contaminants efficiently and are generally used in industries. Bed design is crucial for achieving effective contaminant removal. Reducing particle size results in increased mass transfer rates resulting in small mass transfer zones and more effective utilization of adsorbent bed. But challenges related to high pressure drop are encountered with small particles that would effectively stop operation specially when flow through the bed is gravity driven. To overcome the limitations associated with small particles, a potential solution involves coating inert beads with adsorbent particles on the outer surface. The experimental study outlined in this paper provides valuable insights into the practical implications of these design considerations, offering a pathway for enhancing treatment efficiency and addressing challenges effectively.

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C H A P T E R -1

INTRODUCTION

Introduction

Increase in population coupled with extensive use of various metals in different industrial and household activities had led to the accumulation of various heavy metals in the environment. The quality of these wastes depends on their source, the way in which they are collected, and the treatment they receive. Although some of these heavy metals in traces play significant role in human metabolic system, they are toxic in higher concentration. Heavy metals are of great concern since these are non- biodegradable. These metals could be dispersed in water and accumulate in plants and animals. It causes serious health hazards to human beings through the food chain or by consumption of contaminated water [11].

The resources embedded in the approximately 330 km^3/year of municipal wastewater that is globally generated would be theoretically enough to irrigate and fertilize millions of hectares of crops and to produce biogas to supply energy for millions of households. However, only a tiny proportion of these wastes is currently treated, and the portion which is safely reused is significantly smaller than the existing direct and especially indirect use of untreated wastewater, which are posing significant potential health risks. Wastewater production globally is expected to increase by 24% by 2030 and 51% by 2050 over the current level.

Chromium is one of the most abundant elements found on the Earth's crust. The most common forms are chromium(0), chromium(III), and chromium(VI). Chromium(III) occurs naturally in the environment and is an essential nutrient. Chromium (VI) is the most water soluble and easily enters the living cells. Chromium(VI) and chromium(0) are generally produced by industrial processes. The metal chromium, which is the chromium (0) form, is used for making steel. Chromium(VI) and chromium(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving [13]. These two redox states are characterized by markedly different chemical behavior, bioavailability, and toxicity.

Hexavalent chromium may exist in the aqueous phase in different ionic forms depending on pH. The hydrolysis of Cr^{6+} produces only neutral and anionic species such as chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$). The relative proportion of these species depend on both pH and the total concentration of chromium(VI) [14]. The following equilibrium may be written for the Cr(VI) anions present in aqueous solution

$$H_2C_r\,O_4 \rightarrow HC_r\,O_4^- + H^+ \qquad k_1 = 1.21 \qquad (1.1)$$

$$Cr_2O_7^{2-} + H_2\,O \rightarrow 2HC_rO_4^- \qquad k_2 = 35.5 \qquad (1.2)$$

$$HC_rO_4^- \rightarrow C_{r_2}O_4^{2-} + H^+ \qquad k_3 = 3 \times 10^{-7} \qquad (1.3)$$

$HC_rO_4^-$ is the most dominant form within the pH range of 2 to 6, since $H_2C_r\,O_4$ is deprotonated at pH > 1, whereas $C_r\,O_4^{2-}$ only exist in solution above pH 6. The dangers posed by the toxicity of Cr (VI) are increased by its occurrence as an oxyanion that is only weakly adsorbed by mineral surfaces [1.5]. It does not form a stable (oxyhydr)oxide, and as a consequence Cr(VI) is highly mobile [16, 17].

Chromium(VI) compounds are more toxic than Cr(III) due to their high water solubility and mobility. The most soluble, mobile and toxic forms of hexavalent chromium in soils are chromate and dichromate. The hexavalent form is rapidly reduced to trivalent chromium under aerobic conditions [19].

Chromium and its compounds have various applications in industries such as electroplating, leather tanning, pigment manufacture, metal finishing, water cooling, pump producing, ore and petroleum refining processes. Hexavalent chromium is of particular concern due to its carcinogenic and mutagenic effects. It may cause damage to kidney, lungs and ulceration to skin and is involved in causing birth defects, reduces reproductive healthiness and may cause death, if ingested in high concentrations.

According to the World Health Organization (WHO) and BIS (Bureau of Indian Standards) drinking water guideline, the maximum allowable limit for Chromium (VI) is 0.05mg/L and for discharge into surface water is 0.1 mg/L. [11] . In view of this toxicity and its related

environmental hazards, the level of chromium in wastewater must be reduced below the permissible limit before being discharged into water bodies.

1.1 Methods of Chromium Removal

To meet environmental regulations, effluents or water contaminated with heavy metals must be treated before discharge. Several technologies are available for the removal of chromium species from wastewater. They are mainly:

- Reduction and Precipitation/Coagulation-Flocculation
- Ion Exchange
- Membrane Separation
- Electro dialysis
- Solvent Extraction
- Biological Treatment
- Adsorption

1.1a Reduction- Precipitation Method or Coagulation-Flocculation

This is the conventional method of treatment of wastewater containing Cr(VI). It involves chemical reduction of Cr(VI) to Cr(III) by SO_2 , Na_2SO_3, $FeSO_4$, followed by precipitation of $Cr(OH)_3$ The sludge formed is separated by settling or filtration. The drawbacks of this technique are sludge disposal, and difficulty of recovery of metals from sludge.

1.1b Ion Exchange

Ion exchange is a process involving the exchange of contaminant between the liquid phase for harmless ions present in the solid phase (resin) [11-14]. When all the exchanged sites have been filled with the contaminant ion, the ion exchange resin bed is exhausted. Although all anion exchange resins strongly prefer Cr(VI), the instability of ion exchange resins due to oxidation by Cr(VI) significantly influences run length. The recovery is always less than 100% and was attributed to the reduction of Cr(VI) to Cr(III) with subsequent precipitation of greenish solid $Cr(OH)_3$precipitant. These low recoveries may limit the economic effectiveness of ion exchange as a technique for chromate removal.

1.1c Membrane Separation

Reverse Osmosis (RO) and Nanofiltration (NF) are pressure driven separation processes in which a membrane serves as a barrier that restrains dissolved solute but allows water to pass through. RO and NF uses two distinct mechanism for Cr(VI) removal:

Electrostatic repulsion, which is the rejection of ions by the membrane owing to the charges of the species, and

(ii) Physical straining, which is the rejection of molecule that are larger than the membrane pore size.

The predominant removal mechanism in NF is electrostatic repulsion. The anionic character of Cr(VI) is the fundamental reason that NF could be effective for Cr(VI) removal [15,16]. Chromium oxidation state is less important for RO [17] performance because the pores are so small that chromium molecules are hindered from passing through the membrane by their size alone. However, the membranes are relatively expensive both to procure and to operate. The use of elevated pressure makes this technique costly and sensitive to operating conditions.

1.1d Electro dialysis

In this process, heavy metals are separated through the use of semi- permeable ion selective membranes. Application of an electrical potential between the two electrodes cause a migration of cations and anions towards respective electrodes. The disadvantage is the formation of metal hydroxides which clog the membrane, and operating cost.

1.1e Solvent Extraction

In this process two immiscible liquids are vigorously mixed to disperse one in the other so that solute can migrate from the aqueous solution to the solvent. The organic chelating agents dissolved in solvent react with the ions at the interface to form uncharged complexes that are highly soluble in organic solvent.

1.1f Biological Treatment

Biological treatment could significantly reduce the costs for chemical and energy compared with conventional physical and chemical treatment. There are still some problem in applying this technology to the real wastewater treatment process, such as low biological

reducing rate compared with the high generation rate of wastewater, cell death by high concentration of Cr(VI), the high cost of a bioreactor system, continuous supply of costly nutrients and difficulty in separation of cells after treatment.

Most of these methods were found unsuccessful towards the Cr(VI) removal, if the concentration is below 100 mg/L [1.18]. Few process are of high cost due to the equipment and monitoring system used, while others are sensitive to the characteristic of wastewater such as pH and concentration of Cr(VI).

1.1g Adsorption

The process of adsorption implies the presence of an adsorbent solid that binds the molecule by physical attractive forces, ion exchange, and chemical binding. Adsorption is found to be simple, cost effective and a versatile method for removing heavy metals. In addition, adsorption can remove heavy metals to a lower level than precipitation over a wide range of pH. Adsorption using activated carbon has been considered as a potential technique for the removal of toxic heavy metals. However, the high cost of commercial activated carbon makes the adsorption an expensive one. Therefore, it is desirable that the adsorbent is available in large quantities, easily regenerable, and cost effective for treatment of Cr (VI) contaminated wastewater.

1.2 Bio sorption

It was only in the 1990s that a new scientific area namely biosorption developed that could help to recover heavy metals from aqueous solution. Biosorption has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules. Biosorption process involves a solid phase and a liquid phase containing the dissolved species to be removed. Biosorbents can be alive or dead biomass. However, in practical applications, use of nonliving biomass is more convenient and practical because living biomass cells often require addition of fermentation media, which increases the biological oxygen demand (BOD) or chemical oxygen demand (COD) in the effluent. In addition, non-living biomass is not affected by toxicity of the metal ions and can be subjected to different chemical and physical treatment techniques to enhance their performance. Adsorbed metals can be easily recovered from the biomass by many chemical

and physical methods, so they can be used repeatedly used and give better process economy. Biosorption is a promising process that can reduce capital costs by 20%, operational costs by 36% and total treatment costs by 28%, compared with conventional systems [1.19]. The major advantages of this technique include

- High efficiency in removing heavy metals from dilute solution
- Easy handling
- Low operating cost
- Removal of heavy metals from effluent irrespective of toxicity
- Short operation time and no production of secondary compounds which might be toxic
- With proper selection of eluent, metal recovery is possible
- High possibility of biosorbent regeneration and reuse over a number of cycles

Because of these manifold advantages, biosorption of heavy metals is the most promising separation and purification method from industrial wastewater. The process is generally suited for a wide variety of wastewater with low concentrations of heavy metals.

1.3 Biosorbent Material

A number of other factors influence the choice and viability of natural materials as biosorbents. Availability is a major factor that needs to be taken into account in the selection of biomass. The economy of environmental remediation dictates that the biomass must come from nature or has to be a waste material. Cost is a very important factor when considering materials for use as biosorbents. It is generally recognized that a material can be deemed ‘low-cost’ if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry. Other factors are metal selectivity and regeneration of the biomass for further use. An active agent used for the recovery of metals from solution should fulfill the following criteria:

- Uptake and release of metal should be efficient and rapid.
- Active biosorbent agent should be produced at a low cost and reusable.

- Biosorbent material should have desirable particle size, shape, and mechanical properties for use in continuous flow (mixed, packed bed or fluidized bed) system.
- Sorbent should be metal selective, if desirable, in order to separate specific single metals from a solution containing various metallic species.
- Loss of adsorbent should be minimal.

CHAPTER-2

LITERATURE REVIEW

A. Verma [16] experimentally analyzed the adsorption of hexavalent chromium using an adsorbent from waste tamarind hull. The adsorption process was found to follow a pseudo-first-order rate mechanism. The adsorption capacity increased with temperature, with an equilibrium adsorption capacity of 70 mg/g at 30°C and 81 mg/g at 50°C. The adsorption process was found to follow a pseudo-first-order rate mechanism, with the Freundlich, Redlich–Peterson, and Fritz–Schlunder isotherm fitting the equilibrium data satisfactorily.

Suresh Gupta [17] investigated the use of tamarind seeds as an adsorbent for removing toxic heavy metals like chromium (VI) from wastewater. The adsorbent, activated with concentrated sulfuric acid, showed significant capacity for adsorption. The study tested the adsorption process using Langmuir and Freundlich isotherm models, with the Langmuir isotherm model yielding the maximum adsorption capacity of 11.08 mg/g. The adsorption of chromium (VI) was found to be maximum at low pH values.

Senthil Rajan M [18] used locally available tamarind fruit shells (TFS) pre-treated with 1N H3PO4 to remove hexavalent chromium (Cr^{6+}) from aqueous phase. The system was optimized using a continuously mixed batch reactor (CMBR) under room temperature. The adsorbent showed the highest efficiency (99.1%) in removing $Cr^{6+}$from the aqueous phase. The density and mechanical properties of treated and untreated composites increased with particle size decrease, while water absorption percentage and void content decreased. The biosorption kinetics of Cr^{6+} were modeled using integrated rate expression and second-order rate constants were determined for different Cr^{6+} concentrations. The uptake of Cr^{6+} was well described by the Freundlich isotherm for different biosorbent sizes. The desorption study was significant at 0.5 H_2SO_4.

Apsara V H [19] explored the biosorption of chromium(VI) ions from crude tamarind fruit shells (CTFS) and HCl-treated tamarind fruit shells (H-TS) from aqueous solutions, comparing their extent and evaluating the impact of pH, initial metal ion concentration, and adsorbent dosage. In their study they observed that adsorption of heavy metals is highest at low pH and decreases with increase in pH due to decrease in electrostatic force

of attraction. Low pH increases removal of hexavalent chromium due to hydronium ion adsorption and also the removal of chromium decreases with initial concentration increase, with maximum removal 68 % occurring at a lower concentration of 0.125N at all pH levels.

N. Ahalya [20] discussed the use of tamarind pod shells, discarded as waste, for biosorption of chromium (VI) from aqueous solutions. The study examines parameters like agitation time, adsorbent dosage, and pH, and finds that hydroxyl, carboxyl, and amide groups are involved in the uptake of VI. The study reveals that the biosorption of Cr (VI) on tamarind shells reaches equilibrium at 60 minutes for all concentrations studied. Biosorption of Cr (VI) was noted to depend on the metal solution's pH, with maximum adsorption at 2 and $HCrO_4^-$ being the dominant form.

G S Agarwal [21] study and evaluated the effectiveness of low-cost agro-based materials like Tamarindus indica seed (TS), crushed coconut shell (CS), almond shell (AS), ground nut shell (GS), and walnut shell (WS) for removing Cr(VI). The hexavalent chromium sorption capacity followed a sequence, and tamarind seed was chosen for detailed sorption studies. Sorption kinetic data showed equilibrium conditions within 150 minutes under mixing conditions. Hexavalent chromium sorption decreased with pH and slightly with ionic strength. Cr(VI) removal by TS was mainly chemisorption. They found that the removal of Cr(VI) ions by tamarind seed significantly decreased with increase in pH, slightly decreased with increase in ionic strength and increased with increase in temperature. The Cr(VI) removal appears to be mainly by chemisorption. Desorption of Cr(VI) from TS was partially achieved under alkaline conditions. It was noted that larger sorbent sizes showed lesser removal due to decreased surface area for adsorption. This is in line with adsorption/ion exchange processes where smaller particles increase the rate of metal uptake.

Luis Cabatingan [10] studied that the biosorption of chromate in industrial wastewater is limited by biosorbents' low chemical stability and poor renderability. The optimal condition for chromate biosorption is around pH 2, and electrochemical reduction occurs in parallel with biosorption. Factors influencing equilibrium and kinetics include biomass

amount and total chromate concentration. Desorption of chromate bound by the seaweed is difficult without reducing hexavalent chromate into trivalent chromium.

Lubna.C.H [22] investigated the capacity of adsorbing chromium (VI) from wastewater using tamarind shell as an adsorbent. The study investigated the effects of various parameters on the adsorption process, including pH, contact time, adsorbent dosage, and initial concentration. The maximum removal of chromium was achieved at 150 minutes of agitation, pH 2, and initial concentration of 10 mg/l.

Srinivasa R. Popuri [23] investigated the adsorption of chromium ions from aqueous solutions on crude tamarind fruit shells, treated with HCl and oxalic acid. The biosorbent was characterized using FTIR, EDXRF, and porosimetry. The results show first-order kinetics, and equilibrium data fit well to Langmuir and Freundlich isotherm models. Tamarind shells are excellent sorbents for removing chromium ions due to their outstanding capacities.

Industrial adsorption processes are typically carried out in fixed-bed or packed-bed adsorption columns and mixer settler.

2.1.1 Fixed bed Column

The fixed bed is a vertical column that is packed with adsorbent. The fluid to be treated or separated is introduced at the top of the column and flows downward through the packed bed. Removal of the targeted species occur as it diffuses from the solution to the adsorbent. The treated solution is collected from the bottom of the column. The adsorbent becomes loaded as time progresses with fluoride ions. Eventually breakthrough point is reached and the pollutant start to emerge in the effluent in significant amount.

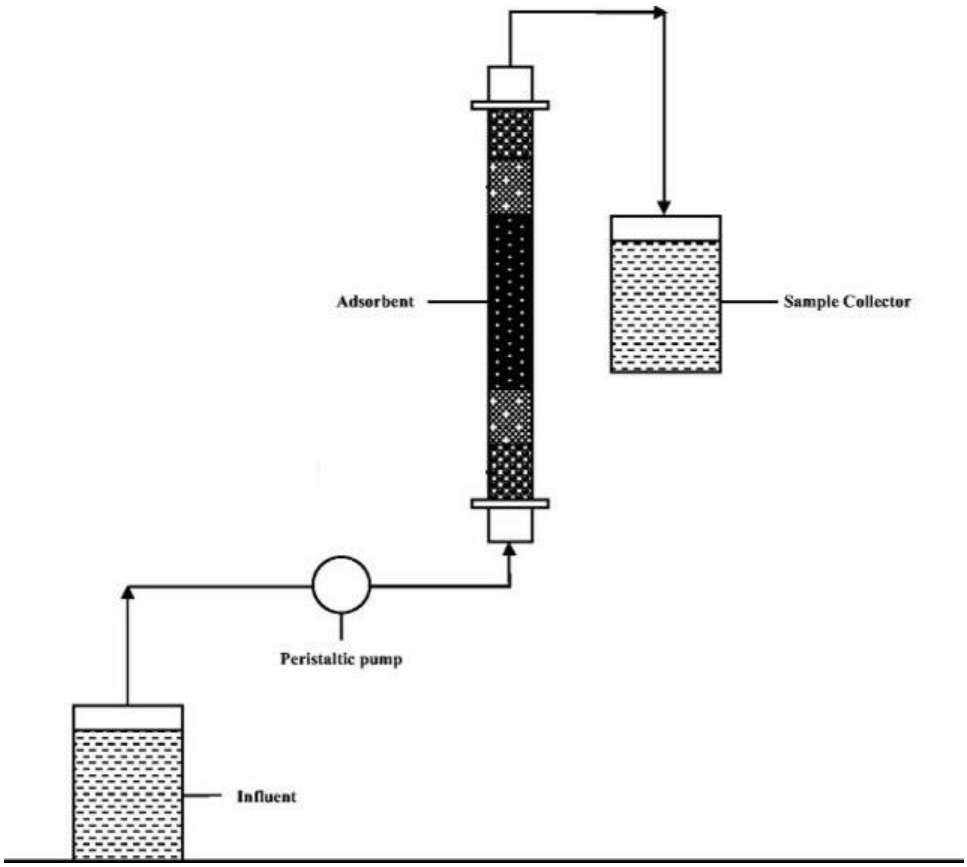


Figure 2.1: Schematic Diagram of a Packed Column

2.1.2Mixer Settler

The typical mixer settler schematic diagram is represented in Figure 2.2. In adsorption process involving a mixer-settler, the mixer phase represents the point where the solution containing the pollutant is mixed with the adsorbent. Inside the mixer compartment, the liquid blend is vigorously stirred or mixed to ensure proper interaction between the liquid phase and solid adsorbents. Following the mixing phase, the merged liquid portions enter the settler chamber, where gravitational forces facilitate the separation. Typically, the denser adsorbent-loaded liquid settles at the bottom, while the clarified liquid ascends to the upper part.

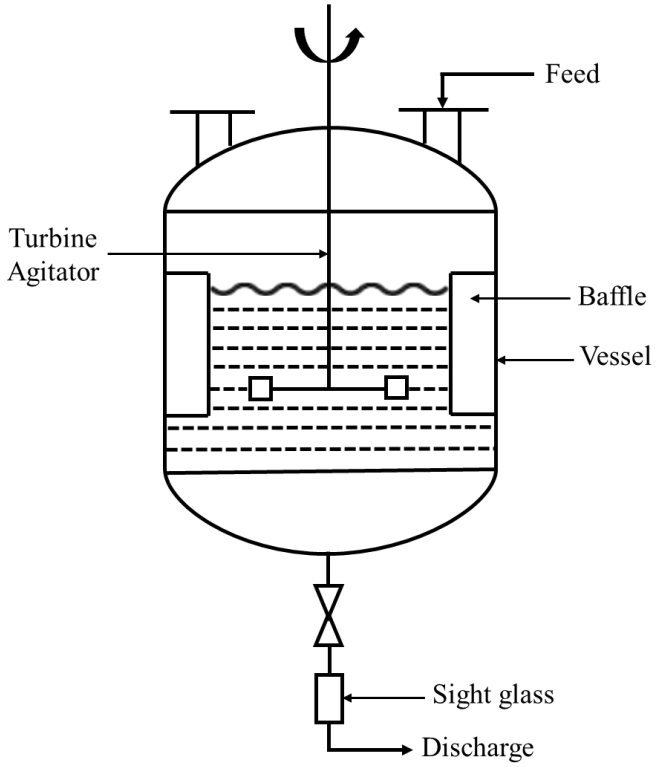


Figure 2.2: Schematic diagram of a Mixer Settler

C H A P T E R -3

AIMS & OBJECTIVES

One of the current challenges of wastewater treatment is the presence of recalcitrant pollutants which are difficult to remove using conventional treatment technologies. This poses a threat to environmental sustainability and hinders the efforts of many industries to adopt cleaner production through zero discharge and subsequent needed to address this challenges. Among all these methods, the process of adsorption proved to be the most effective technique for the removal of Cr(VI) from wastewater. Adsorption has advantages over other methods because of simple design and involve low investment in term of both initial cost and land required. The adsorption method of certain undesirable toxic materials such as heavy metals on various adsorbents may be performed in a laboratory using either batch mode or adsorption techniques for fixed bed columns. Batch laboratory adsorption studies can be helpful to determine conditions for maximizing equilibrium capacity and adsorption rate for removing specific pollutant components [19]. On the other hand, continuous column studies provide the most practical use of the adsorption technique in the treatment of wastewater. The continuous adsorption method is more appropriate and suitable in real water treatment industries because of its low operating costs and the ability of columns to adapt to versatile processes.

In recent years, the search for low-cost adsorbents that have pollutant –binding capacities has intensified. Materials locally available such as natural materials, agricultural wastes and industrial wastes can be utilized as low-cost adsorbents.

The aim of researchers dealing with sorption was to explore new and low-cost sorbents for metal ions adsorption. Hence, a number of low-cost and abundantly available agricultural wastes have been tried as adsorbents for the removal of chromium Cr(VI) from wastewater [9]. Some of them are rice husk [10], bagasse [11], wheat straw [12], saw dust [13,14] and various other low-cost biological wastes [15]. Tamarind shell or hull is an easily available agricultural waste material and has been used in this study

3.1.1Advantage and Disadvantage of Small particles in adsorption process:

The rate of intra particle diffusion is higher in small particles compared to larger particles, even when both types of particles possess identical porosities as has been reported by previous investigators. This phenomenon can be attributed to the increased surface area-to-volume ratio of smaller particles, smaller diffusion path within the particle and higher external phase mass transfer coefficient.

The faster mass transfer rate ensures that the smaller particles are saturated as compared to larger particles. This results in more efficient use of the particles delaying the breakthrough time and longer use of the adsorbent bed.

However, small particles with a wide size distribution are present, tend to form clusters and agglomerates, which reduces their overall surface area available for interaction with the liquid phase. As a result, dispersion is hindered, leading to less efficient mixing and slower mass transfer rates. These findings have implications for various industrial processes, such as chemical reactions and wastewater treatment, where efficient mixing and mass transfer are crucial for optimal performance.

3.2.My proposal:

The reduction in mean particle diameter result in increased surface area, shorter diffusion path length within the matrix and improved accessibility for adsorbate molecules, allowing for more efficient adsorption. To maximize outlet efficiency, utilizing smaller particles can be a viable option. However, it is important to consider the potential drawbacks that come with using smaller particles. In the case of packed beds, smaller particles can lead to increased pressure drop and reduced flow capacity, which may hinder overall system performance.

To eliminate the demerits of fine adsorbent particles, it is proposed that fine adsorbent particles be attached to outer surface of inert particles. This innovative approach allows for a higher resultant velocity through the bed compared to using fine particles alone.

This innovative approach addresses the limitations of small particle beds and offers scope of improved performance in various applications. By incorporating this design, the efficiency and effectiveness of the bed are significantly improved, leading to enhanced performance and productivity. This advancement in particle bed technology showcases the continuous efforts in finding solutions that address the limitations and challenges associated with small particle systems and also this advancement is a significant step towards improving efficiency and optimizing processes that rely on small particle beds.

In this tamarind fruit shell (TFS) and commercial activated carbon was used as the adsorbent for removal of hexavalent chromium from aqueous solution. Equilibrium studies were performed to determine the maximum capacity of these adsorbents. Fixed bed studies were carried out for continuous removal of hexavalent chromium. The bed was constituted of TFS crushed into fine powder and coated onto inert beads. Breakthrough curves provide insight into the efficiency of the adsorbent bed. Therefore, breakthrough curve characteristics were studied with variation of operating conditions such as flow rate, pH, feed concentration and bed height.

CHAPTER 4

MATERIALS AND METHODS

4.1 Materials

4.1.1Chemicals Used:

Names of the chemicals used for the present work has been tabulated in TABLE 4.1

TABLE 4.1

Name	CAS Number	Company
Potassium Di chromate(K_2CrO_7)	7778-50-9	Merck
Diphenyl carbazide (DPC)	140-22-7	
Sulfuric acid (H_2SO_4)	10233-01-9	
Hydrochloric acid (HCL)	7447-40-7	
Acetone	4251-29-0	

4.1.2 Equipment's Used:

Names of the equipment used for the present work has been tabulated in TABLE 3.2

TABLE 4.2

Name	Specification	Company
Weighing balance	BSA224S-CW	Satorius
Hot Air Oven	-	Carbolite Gero & Kanthal
Magnetic Stirrer	-	Remi
UV-1800 Spectrophotometer	UV180ENG240V,SOF	Shimadzu
Peristaltic pump	-	Labman

4.1.a. Preparation of Tamarind Fruit Shell bio sorbent:

Tamarind fruit shells, which are typically discarded after the extraction of tamarind pulp, were gathered from tamarind trees in their natural habitat. These discarded shells were carefully cleaned using double distilled water to remove any impurities. It was then subjected to a gentle drying process in an oven set at 60ºC for a duration of 2 hours. The dried biomass was then powdered and sieved to get uniform size. Bio adsorbents of -250 mesh size was used for further studies. Fig. 4.1 is a representation of Tamarind fruit shells bio adsorbent.



Fig. 4.1- Tamarind fruit shells bio adsorbent

4.1.b. Pre-treatment of the biosorbent

The tamarind shells are immersed in 1N hydrochloric acid for a period of 24 hours.

4.1.c. Preparation of potassium dichromate solution:

The chromium solution was prepared by dissolving potassium dichromate, K2Cr2O7 (analytical reagent grade) in double distilled water. The pH was adjusted by using 10% (v/v) sulfuric acid solution.

4.1.d. Diphenyl carbazide solution:

The solution was prepared by dissolving 250 mg of 1,5-diphenylcarbazide in 50 mL of acetone.

4.1.e. Analysis of chromium (VI):

The concentration of hexavalent chromium (Cr(VI)) present in the liquid samples was accurately determined calorimetrically. This was achieved through a specific reaction with 1,5-diphenylcarbazide in an acidic solution, following a standardized method. After the reaction took place, the resulting red-violet sample was subjected to measurement at 540 nm. This measurement was carried out with precision using a spectrophotometer from Perkin-Elmer, specifically the Lambda 25 model.

4.1.f. Equilibrium studies:

Equilibrium experiments were carried out by varying adsorbent dosages from 0.25 g/ml to 1.5 g/ml at 750 rpm maintained at a room temperature. The results obtained from the equilibrium study have been reported in terms of adsorption capacity and were fitted to Langmuir model. Figure 4.2 illustrate the equilibrium curve.

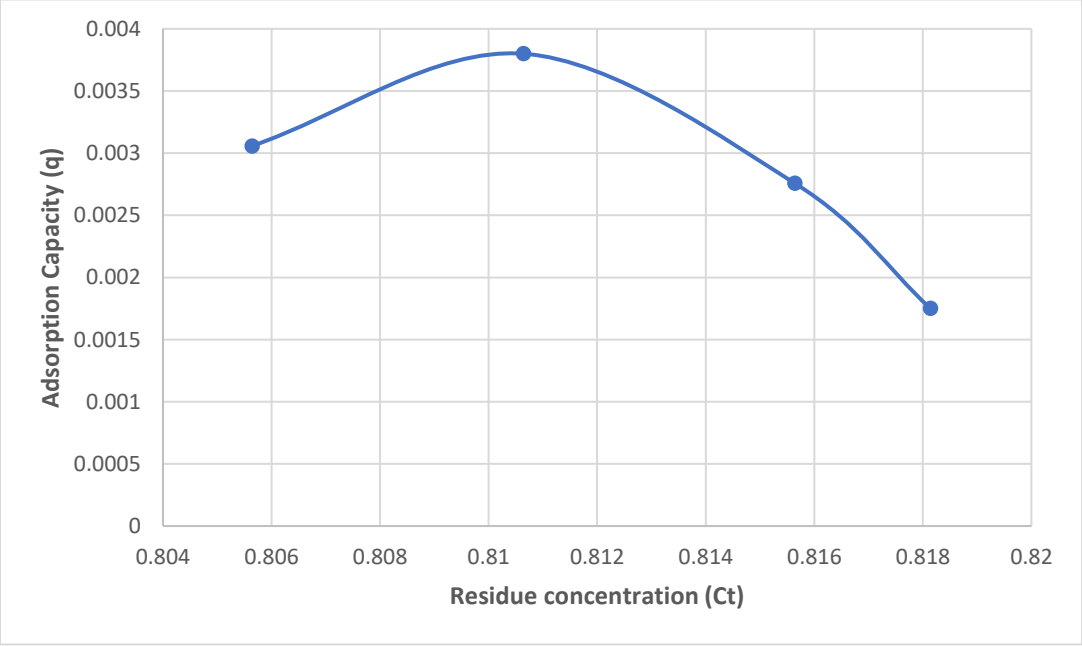


Fig. 4.2- Equilibrium Curve

4.2 Methods:

4.2.a. Preparation of calibration curve:

Measured volumes of a chromium standard solution was transferred into 250-mL beakers or conical flasks, creating standard concentrations ranging from 0.1 to 0.5 mg/L Cr(VI). 95 mL of this solution was transferred into a 100-mL volumetric flask. To this was add 2.0 mL of diphenyl carbazide solution to the flask and contents thoroughly mixed. Sulfuric acid solution was used to achieve a pH level of 2 +- 0.5. Dilute the mixture to a total volume of 100 mL using reagent water and allow it to stand undisturbed for a period of 5 to 10 minutes to ensure complete color development.

An appropriate amount of each solution with color was transferred to a 1-cm absorption cell and absorbance was measured at a wavelength of 540 nm. Water was used as a reference.

To create a calibration curve, the absorbance values was plotted against the concentration of Cr(VI) measured in milligrams per liter (mg/L). The calibration curve is shown in Fig. 4.3.

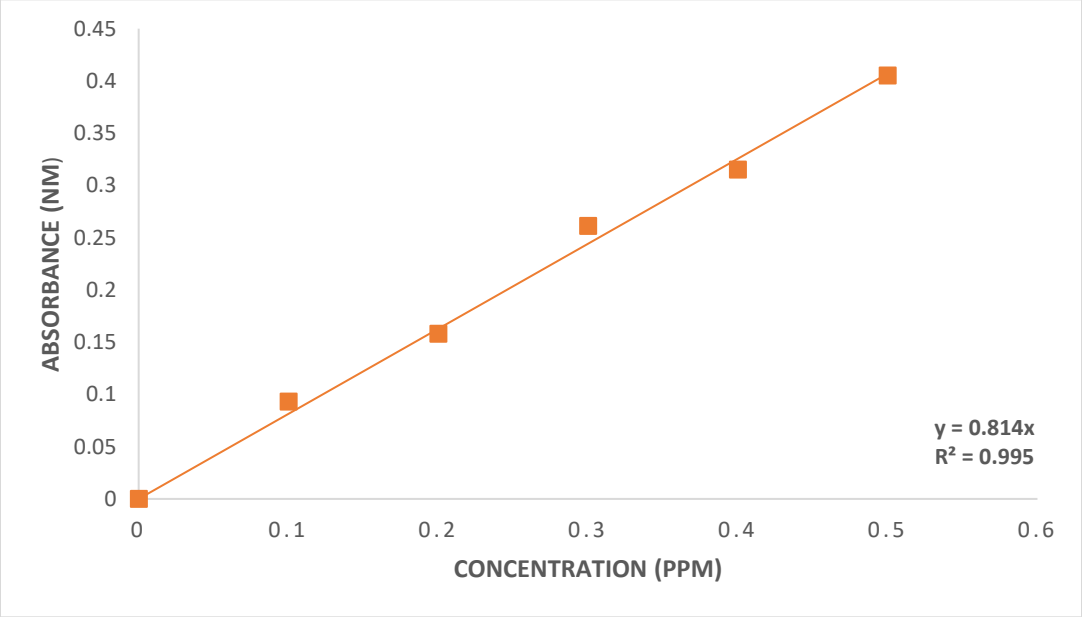


Fig. 4.3- Calibration Curve of analysis of chromium

C H A P T E R 5

EXPERIMENTAL PROCEDURE

5.1. Materials:

5.1.a. Preparation of adsorbent beads:

Adsorption beads are meticulously prepared by a precise procedure to adhere the beads evenly and effectively, creating a high surface area for adsorption. Initially, the beads are carefully placed on a surface that has been pre-covered with epoxy resin that acts as a binding agent, securely holding the adsorbent particles in place. Subsequently, the particles are strategically positioned onto the resin-covered surface of the beads, ensuring a secure attachment. The beads are then gently rolled to guarantee an even distribution of the particles. Then the beads undergo a thorough drying process and the drying process helps to solidify the bond between the nanoparticles and the beads, ensuring their stability and longevity. They are placed in an oven set at 60ºC for a duration of 1 hour. Once the adsorption beads are fully dried, they are ready to be used in various applications. The adsorbent beads are shown in Fig. 5.1 below.

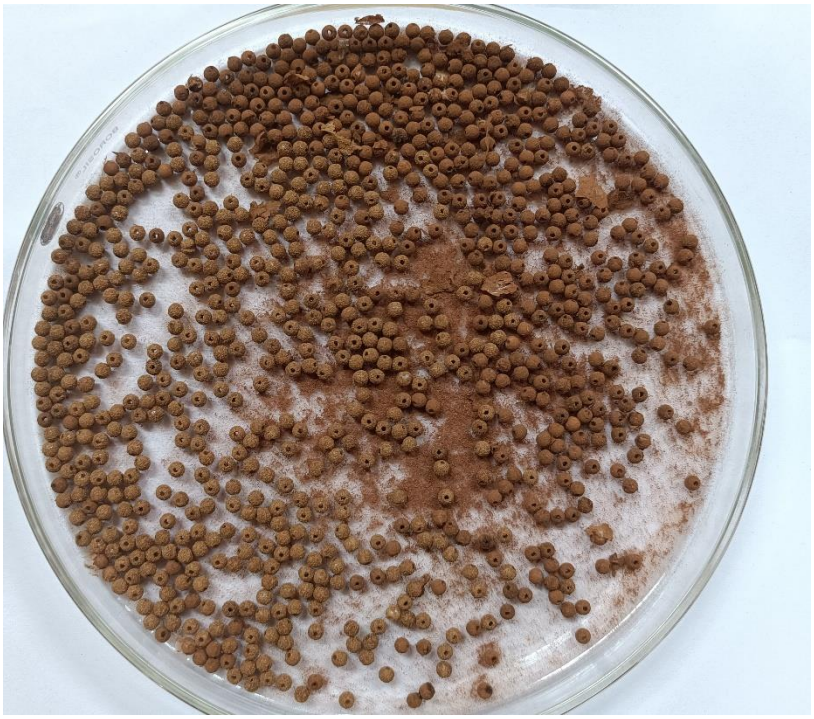


Fig. 5.1- Adsorbent Beads

5.1.b. Preparation of sodium alginate adsorbent beads:

4 gm of Sodium alginate was dissolved in 70 ml of water creating a solution that was continuously stirred for a duration of 1 hour to ensure proper dispersion. Then 2.7 gm of the tamarind fruit shell adsorbent was added into the solution followed by an additional hour of stirring to achieve a well-blended and uniform mixture.

The prepared homogeneous mixture was carefully and gradually released into a 100 ml solution containing 4 gm of $CaCl_2$ via a dropper apparatus, this was meticulously executed to allow for the creation of well-structured and spherical beads and aiming to commence the bead formation process.

Once the bead formation was complete within the solution, the resulting beads were meticulously separated from the medium through a filtration process, ensuring removal of excess solution. Furthermore, this separation was accompanied by repetitive washing cycles using distilled water to guarantee the removal of any residue that might compromise the quality of the beads. Alginate beads is shown in figure 5.2 below.



Fig. 5.2- Alginate beads

5.2 Methods

5.2.1. Experimental Setup:

Continuous experiment was carried out in self-designed packed bed. The set-up consists of two reservoirs, one is for storage the inlet liquid solution and another is for collect the outlet effluents. Peristaltic pump is used for transporting the inlet solution to the packed bed. The schematic diagram of the experimental setup is shown in Fig. 5.3.

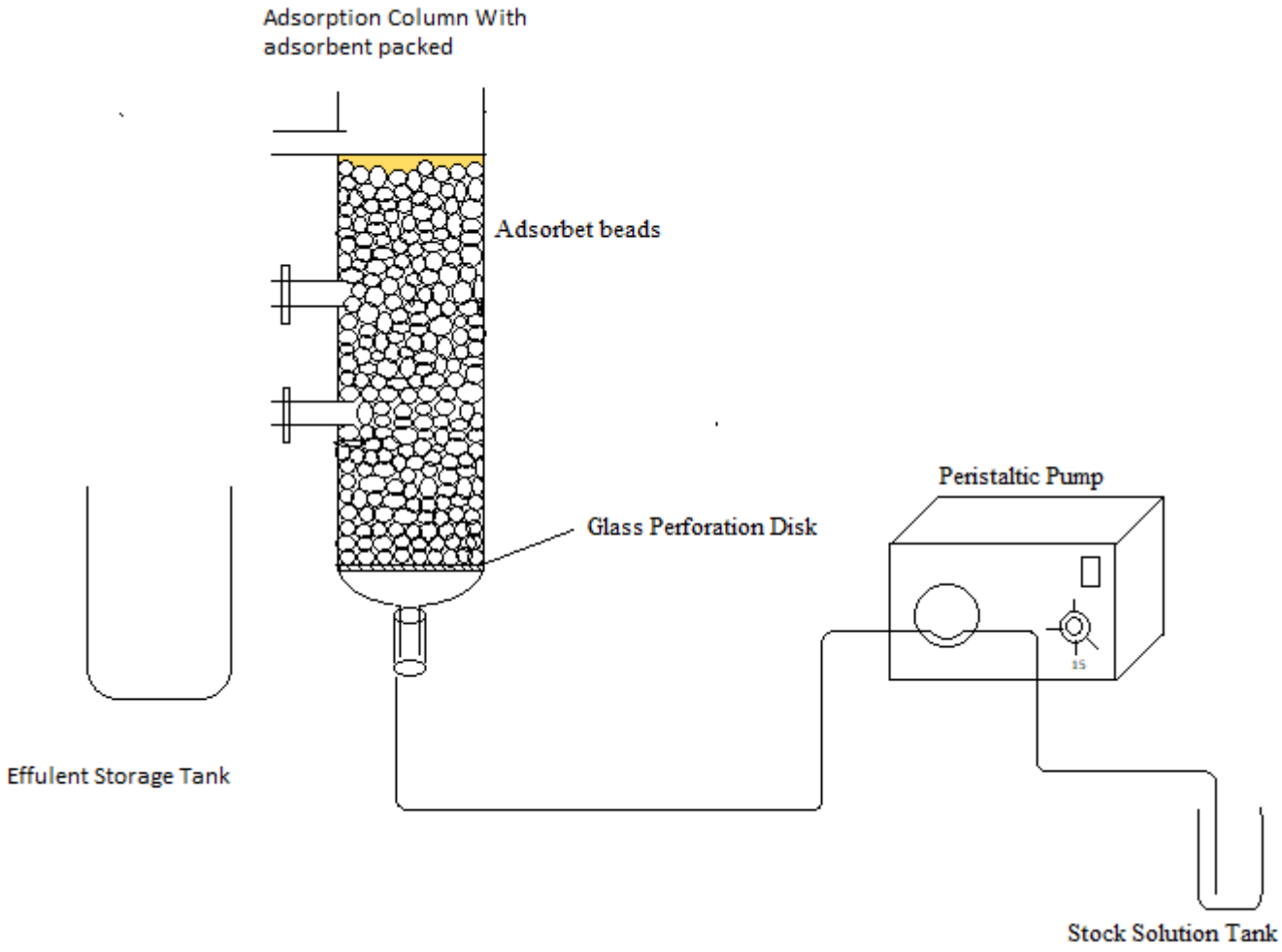


Fig. 5.3- Schematic Diagram of Experimental Set-up

The column is constructed from durable borosilicate glass, known for its high resistance to thermal shock and chemical corrosion. The dimensions of the column are: diameter of 2 cm and a length of 16 cm. Three outlets were located at 8 cm, 12 cm, and 15 cm from the perforation disk allow for the collection from different bed heights. The lower part of the column is specifically designated for the inlet flow of the liquid, allowing for a smooth and controlled distribution. To securely hold the adsorbent in place, a glass perforation disk was incorporated into the bottom of the column to prevent beads from escaping. The experimental packed column shown in Fig.5.4. and packed column filled with adsorbent alginate composite beads are shown in Fig. 5.5.





Fig. 5.4- Packed column with adsorbent beads

Fig. 5.5- Packed column with alginate-adsorbent composite beads

The peristaltic pump, a versatile and reliable device known for its ability to precisely control fluid flow was used to pump the solution into the column.

5.2.2. Experimental Procedure:

- Prior to the experiment, the packed column undergoes a thorough washing process by flushing it with deionized water. By purging the column with deionized water, any potential contaminants are effectively removed, ensuring a clean and stable experiment to take place. This rigorous purification method helps to enhancing the accuracy and validity of the experimental results.
- The column is carefully packed with the prepared tamarind shell adsorbent beads to ensure uniform distribution and prevent channeling or preferential flow paths.
- Chromium (VI) solution with a known concentration is then prepared for the experiment and carefully mixed and analyzed to ensure its accuracy before being used in the experiment.
- The inlet of the column is connected to a reservoir containing the chromium (VI) solution, and the flow is initiated at a controlled rate using a peristaltic pump.
- Effluent samples are collected at regular intervals during the experiment to analyze and determine the concentration of chromium (VI) remaining in the treated solution.
- The experimental set-up is shown in Fig. 5.6.



Fig. 5.6- Experimental set-up

C H A P T E R- 6

CONTINUOUS STUDY IN PACKED BED

6.1. Result & Discussion

The removal of Chromium (VI) using tamarind fruit shells in a packed bed with continuous flow has shown to be a promising method for wastewater treatment. The experiment aimed to evaluate the efficiency of tamarind fruit shells in removing Chromium (VI) from wastewater under different conditions.

The experiment was tested at various pH levels, different bed heights of the packing material, and varying initial concentrations of chromium(VI) solution. The results obtained from these experiments are discussed in detail in the subsequent pages.

6.1.a. Effect of pH:

One of the parameters that strongly affect the sorption capacity is pH. The experiment was carried out at pH 2 and normal pH of the solution (~ 5.5) at constant flow rate of 15ml/min and feed concentration of 10 mg/L and bed height of 15 cm. The amount of adsorbent present in the bed was 2.7 g. The results are depicted in Figure 6.1. The maximum percentage removal of chromium (VI) ions on the adsorbent was observed at pH 2 and significantly decreased at higher pH values. A similar trend was also reported by several researchers [10-11]. It is known that hydrogen chromate ion ($HCrO_4^-$) is the dominant ionic form [11] of Cr (VI) between pH 2-4. This would suggest mono charged ions are more preferentially adsorbed as compared to divalent ions. Better adsorption capacity observed at low pH values due to the large number of H^+ ions present at these pH values. The negative charge of the chromate ions is neutralized onto the adsorbent surface by excess hydrogen ions. The negative charges are generated from oxygenated functional groups such as lactones or hydroxyl groups.

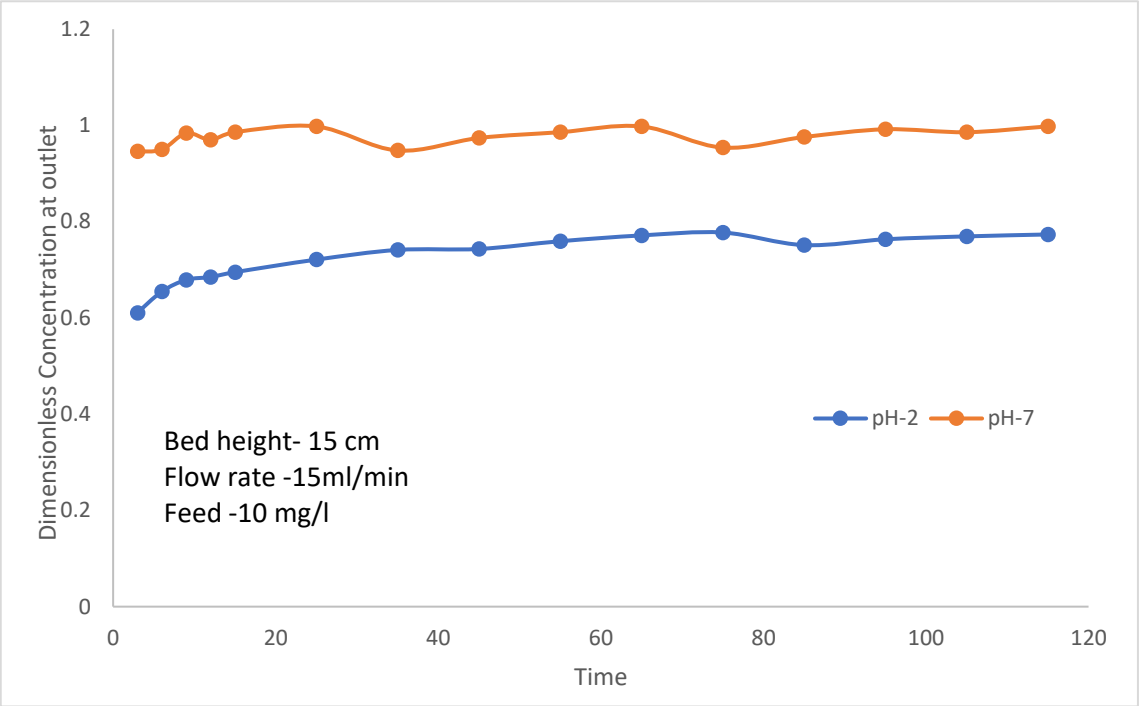


Fig. 6.1. – Effect of pH

6.1.a. Effect of bed height:

The effect of bed height on the breakthrough time was studied at feed concentration 10 mg L^{-1} , pH 2.0 and feed flow rate of 15 mL min^{-1}. Fig. 6.2 represents the breakthrough curves at bed height of 8 and 15 cm. The results showed that the shape and gradient of the breakthrough curve was slightly different with the variation in the bed depth. Higher uptake of chromium (VI) was observed at the higher bed depth. The increase in metal uptake capacities with the increase of bed height in the fixed bed column is due to increased surface area of the adsorbent, which provided more binding sites for the sorption [12].

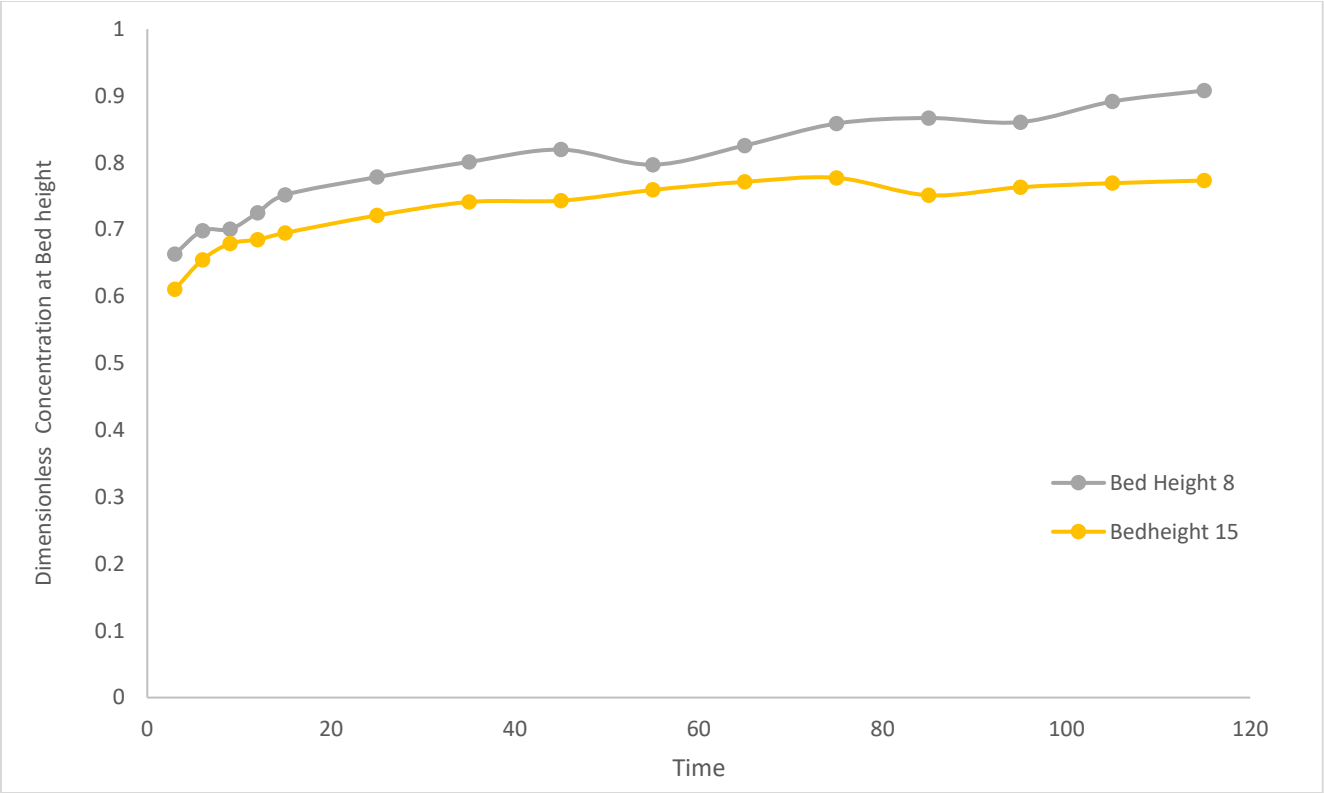


Fig. 6.2 – Breakthrough curves at different bed

6.1.c. Effect of Cr(VI) Concentration:

These experiments were performed with varying initial chromium concentrations (10 and 20 mg/L) at pH 2, feed flow rate of 15ml min^{-1} and bed height of 15 cm. The experimental result are presented in Fig. 6.3 It was observed that chromium removal efficiency decreased with the increase in initial chromium concentration. At lower chromium concentrations, the ratio of the initial mole number of Cr(VI) ions to the available surface area of adsorbent is large. However, when the concentration of Cr(VI) ions is higher, the adsorbent sites available for adsorption.

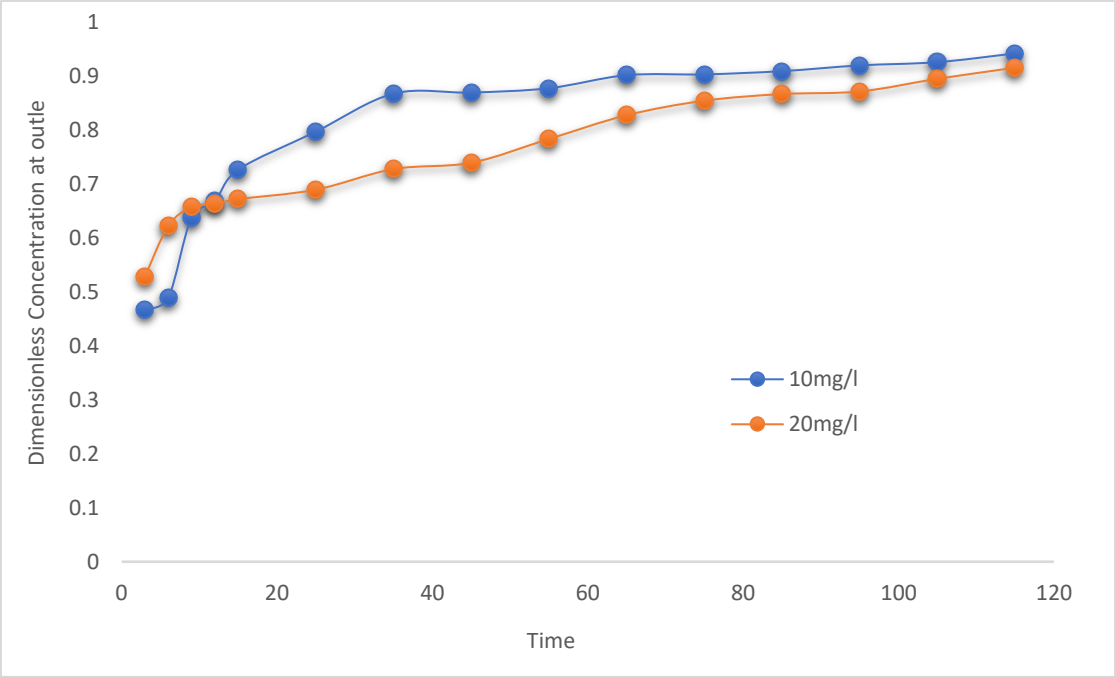


Fig. 6.3 – Effect of Cr(VI) Concentration

6.1.e. Effect of flow rate:

The effect of flow rate in the fixed bed column packed with tamarind fruit shell adsorbent beads was investigated varying the flow rate from 15 and 25 mL min^{-1} with bed depths held constant at 15 cm. The pH and influent chromium concentration in the feed was 2.0 and 10 mg L^{-1} , respectively. It can be seen from Fig. 6.4 that at different flowrates initially the outlet concentrations are similar but after 20 min there is a drop of concentration for the flowrate of 25 ml/min and after that it kept on increasing with a higher rate than 15 ml/min.

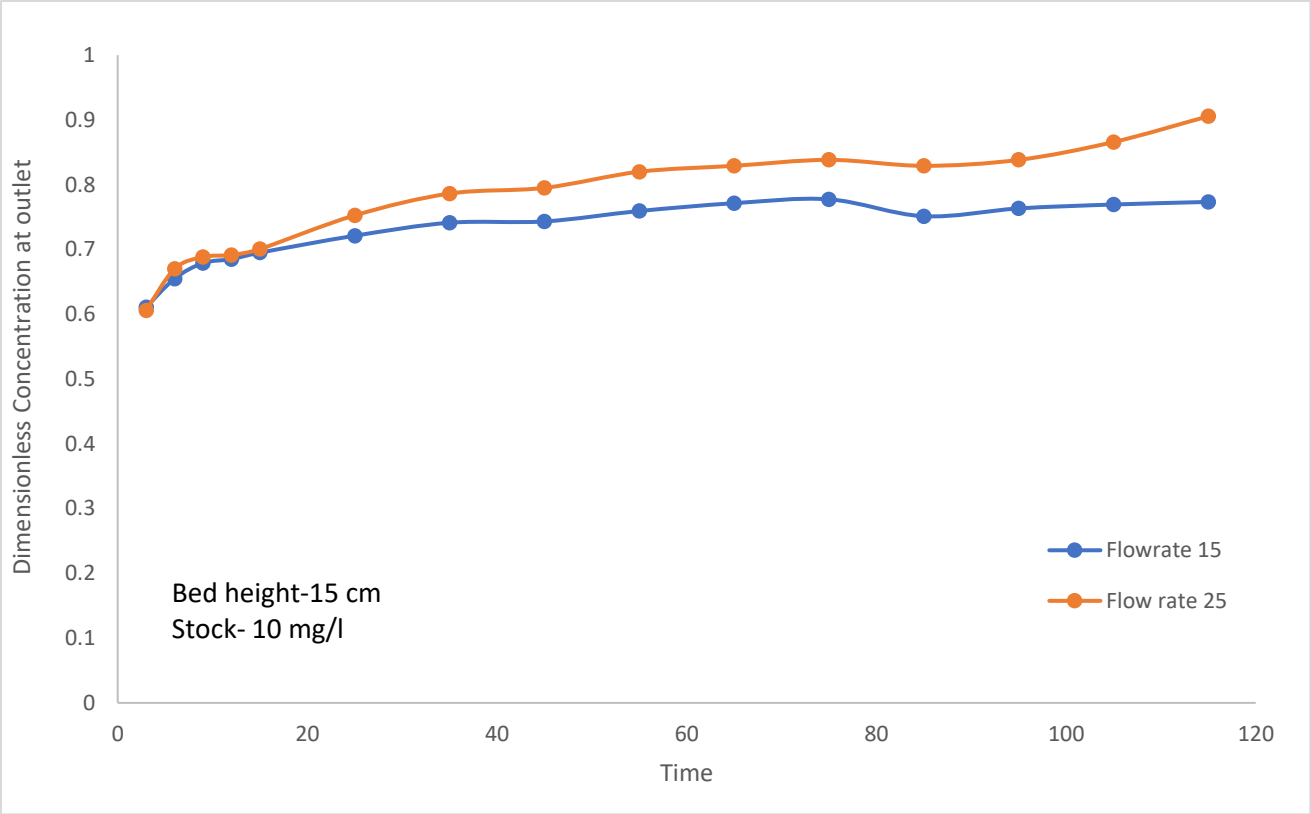


Fig. 6.4 – Effect of flow rate

6.2. Comparison study of adsorbent beads and Sodium Alginate beads:

In this study, breakthrough studies were carried out by impregnating sodium alginate beads with adsorbent particles. The results were compared with a bed were the adsorbent particles were coated outside beads. Figure 6.5 shows the breakthrough curves obtained. The experimental conditions were feed flow rate: 15 ml min^{-1}, feed pH 2, feed concentration 10 mg/1, bed height: 15 cm, amount of adsorbent in bed: 2.6 g. It was observed that when the concentration of Cr(VI) is 10mg min^{-1}, the maximum adsorption efficiency is achieved with adsorbent beads compared to alginate beads. When the adsorbent particles were inside the bed, the chromium ions had to be diffuse through the pores of the alginate beads to reach the adsorbent surface. The intraparticle diffusional resistance lowed the uptake rate resulting in lower adsorption rate.

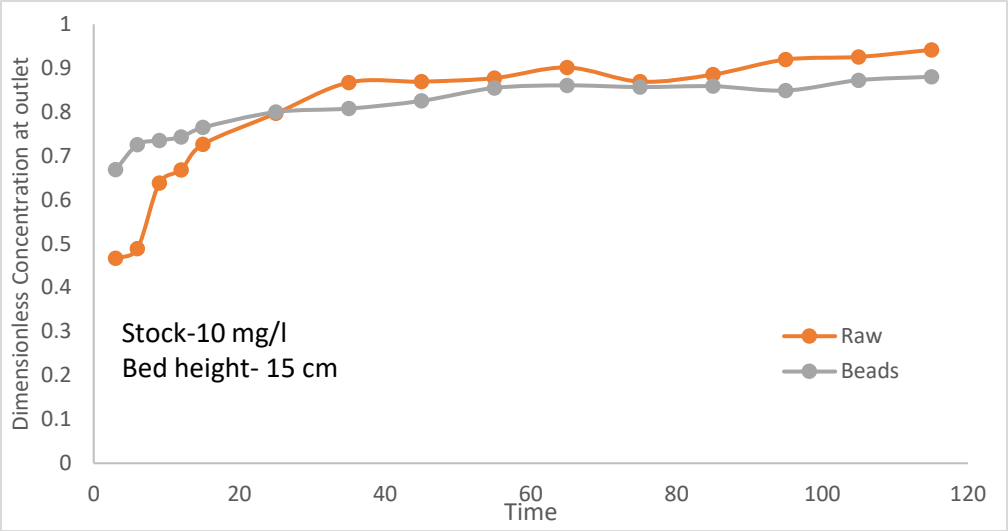


Fig. 6.5. – Breakthrough curve between adsorbent beads and Sodium Alginate beads

6.3. Comparison study of adsorbent beads and raw adsorbent:

A comparative study with bed composed of adsorbent particles (bed height = 2cm) which represent as bed A and adsorbent particles coating the surface of inert particles (bed height = 15 cm) that is represent as bed B was conducted using 2.6 g constant flow rates of 15 ml min^{-1}. The feed pH was maintained at 2, while maintaining a constant bed height of 15 cm. The amount of adsorbent used was 2.6 g. The results are depicted in Fig 6.6.a and Fig 6.6.b for feed concentration of 10 mg L-1 and 20 mg L-1 and maintaining pH 2. It is seen that during the initial period, the removal efficiency of the bed A was higher for both the feed concentration. After sometime, the there was no significant difference in outlet concentration of chromium.

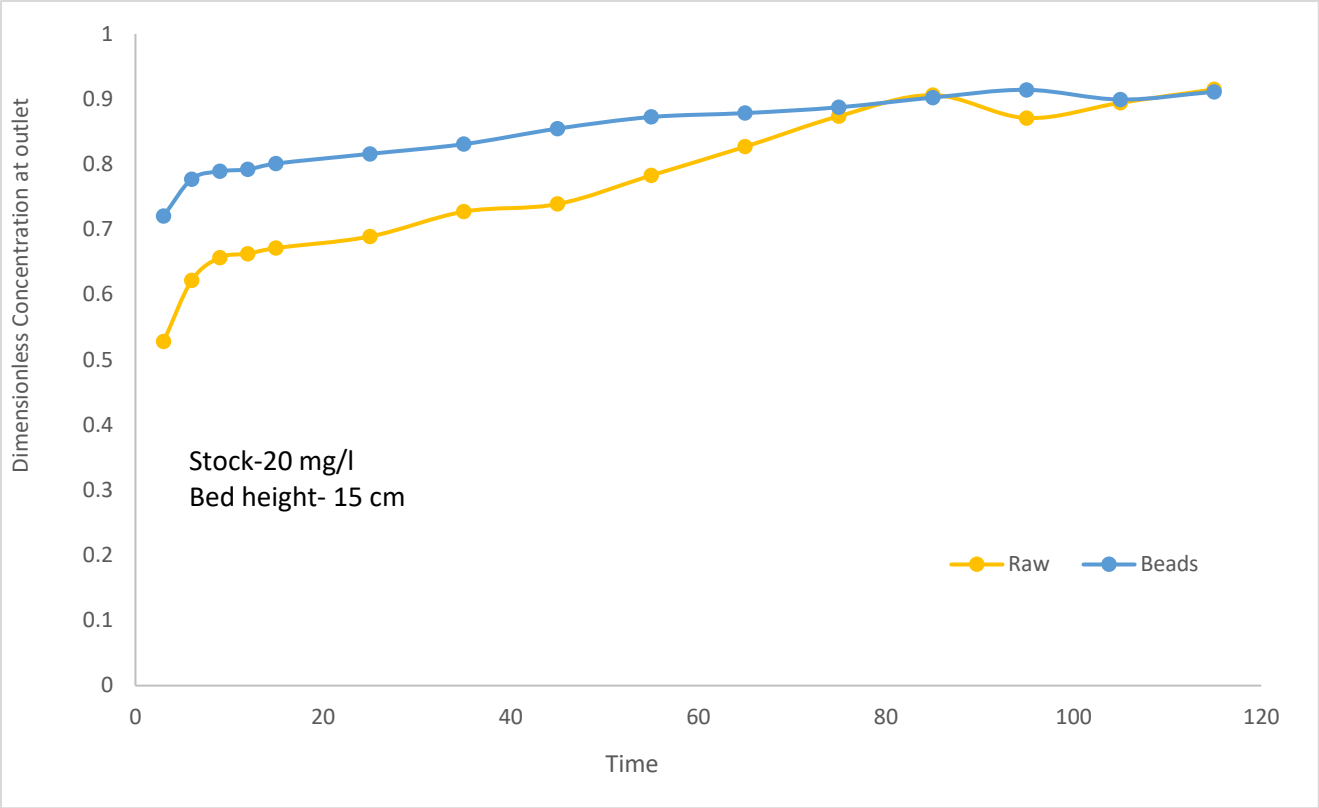


Fig. 6.6. – Breakthrough curve between raw adsorbent and adsorbent beads

C H A P T E R -7

CONTINUOUS STUDY USING COCONUT SHELL

Continuous removal of Cr(VI) was also carried out in fixed bed using powdered activated carbon obtained from coconut shell coated on HDPE granules. The equilibrium results and breakthrough studies are presented in this chapter.

7.1 Materials

7.1.1Chemicals Used:

Names of the chemicals used for the present work has been tabulated in TABLE 7.1

TABLE 7.1

Name	CAS Number	Company
Potassium Di chromate(K_2CrO_7)	7778-50-9	Merck
Diphenyl carbazide (DPC)	140-22-7	
Sulfuric acid (H_2SO_4)	10233-01-9	
Hydrochloric acid (HCL)	7447-40-7	
Acetone	4251-29-0	

7.1.2 Equipment's Used:

Names of the equipment used for the present work has been tabulated in TABLE 7.2

TABLE 7.2

Name	Specification	Company
Weighing balance	BSA224S-CW	Satorius
Hot Air Oven	-	Carbolite Gero & Kanthal
Magnetic Stirrer	-	Remi
UV-1800 Spectrophotometer	UV180ENG240V,SOF	Shimadzu

7.2.1.Preparation of activated carbon:

Carbonization was done after cleaning and crushing the coconut shells into smaller sizes for easy loading into the crucibles. The temperatures at which the carbonization was done is 350^0 C for 4 hrs. The carbonized coconut shells were further crushed using a laboratory mortar and pestle. The samples of carbonized coconut shells were soaked in hydrochloric acid (2% conc.) for 24 hours. The resulting slurry formed from each sample was washed in distilled water until the mixture got to a normal pH and the carbon slurry was reinstated into hot air oven at a final temperature of 80ºC and remove water from the activated carbon and enhance storage. Activated carbon sample is illustrated in Figure 7.1.



Fig. 7.1- Activated carbon sample

7.4. Preparation of adsorbent beads:

The beads are carefully prepared using a precise process to evenly and effectively adhere the beads, resulting in a high adhesion surface area. The HDPE granules are first heated at 100^0C to make the granules softer and act as a resin surface that serves as a bonding agent, holding the adsorbing particles firmly in place. The adsorbing particles are strategically placed onto the sticky granule's surface and hammered to attach to the adsorbent of the surface of the granules. The granules undergo drying at room temperature. The drying

process helps strengthen the bond between nanoparticles and beads, making them more stable and long-lasting. Once fully dried, adsorbing beads are ready for use. The granules-adsorbent beads are shown in figure 7.2.



Fig. 7.2- Granules-adsorbent bead

7.5. Experimental Procedure

- The packed column is washed thoroughly before the experiment. This is done by flushing the column with deionized water. Deionized water removes all contaminants from the column, making the experiment more stable and accurate. This thorough purification process improves the reliability and reproducibility of the experiment.
- The column is filled with the adsorbent beads prepared in the activated carbon coconut shell to ensure uniformity and avoid channeling or preferential flows.
- In order to ensure accuracy, a solution of chromium (VI) at a known concentration is carefully mixed and examined before being used in the experiment.
- A peristaltic pump is used to start the flow of the chromium (VI) solution at a controlled rate from a reservoir that is connected to the column's inlet.
- Throughout the experiment, wastewater samples are taken at regular intervals to measure and quantify the amount of chromium (VI) still present in the treated solution.
- Packed column with activated coconut shell adsorbent are shown in Fig. 7.4.

7.6. Result & Discussion

7.6.1. Effect of pH

Batch equilibrium studies was performed for different levels of initial pH of 1 and 7 for initial feed concentrations of 50 mg/l and at constant adsorbent dose of 1 g/ml. The temperature was maintained at 28˚C and different contact time of 30,60,90 and 120 min. From Fig. 7.5 , it is clear that when the pH is normal the adsorption capacity was increases from, 3.7 to 8.5, and 4.6 to 10.8 for pH 2 in constant concentration of 50 mg/l and maximum adsorption takes place at pH 2 and hence the process will be favorable in a highly acidic medium.

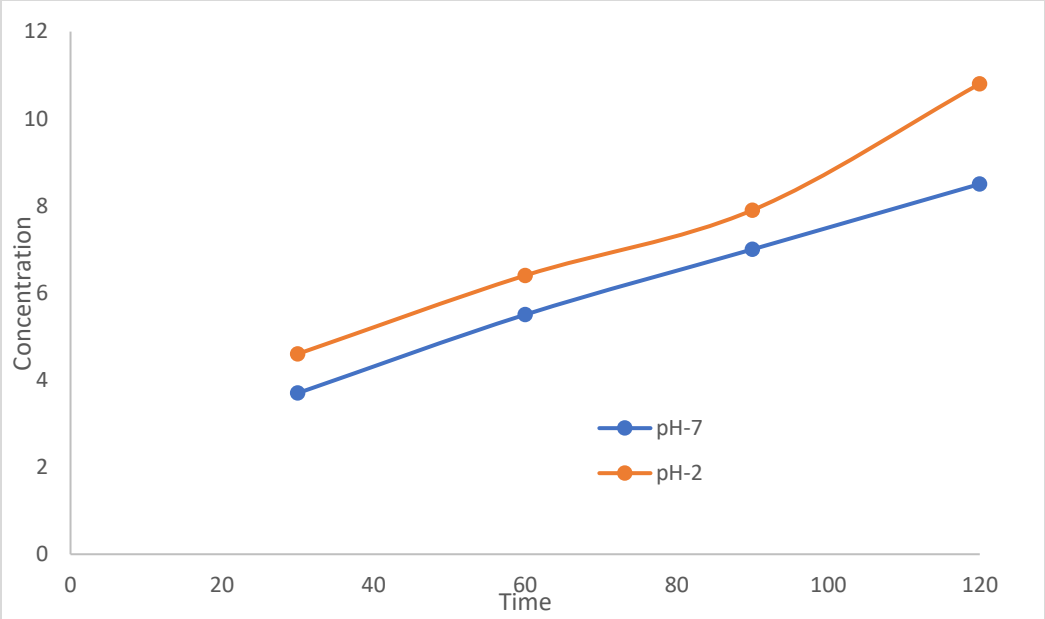


Fig.7.3- Effect of pH

7.6.2. Effect of concentration

The experiment was performed for different initial feed concentration of 50 and 60 mg/l at a constant pH of 2 for adsorbent doses of 1 g/ml. The effect of chromium concentration in the solution on the adsorption is with increased initial feed concentration of chromium (VI), there was a decrease in the adsorption of chromium. The adsorption capacities for chromium (VI) decreased from 0.89 to 0.74 at 60 mg/l concentration and increase to 1.16 to 1.23 when the concentration was 50 mg/l.

7.6.3. Fixed Bed Studies:

The removal of Chromium (VI) using activated carbon coconut shells in a packed bed with continuous flow has shown to be a promising method for wastewater treatment. The experiment aimed to evaluate the efficiency of activated carbon coconut shells in removing Chromium (VI) from wastewater under different conditions.

The experiment was tested at continuous pH levels and varying initial concentrations of chromium (VI) solution. The results obtained from these experiments are discussed in detail in the subsequent pages.

Initial chromium concentrations (50 and 150 mg/L) were varied in these tests, which were carried out at pH 2, feed flow rate of 15 ml min-1, and bed height of 15 cm. Fig. 7.4.a and Fig. 7.4.b presents the results of the experiment. It was found that when the original chromium concentration increased, the effectiveness of chromium removal decreased. The initial mole number of Cr(VI) ions to the accessible surface area of the adsorbent is considerable at lower chromium concentrations. On the other hand, there are more adsorbent sites accessible for adsorption at greater Cr(VI) ion concentrations.

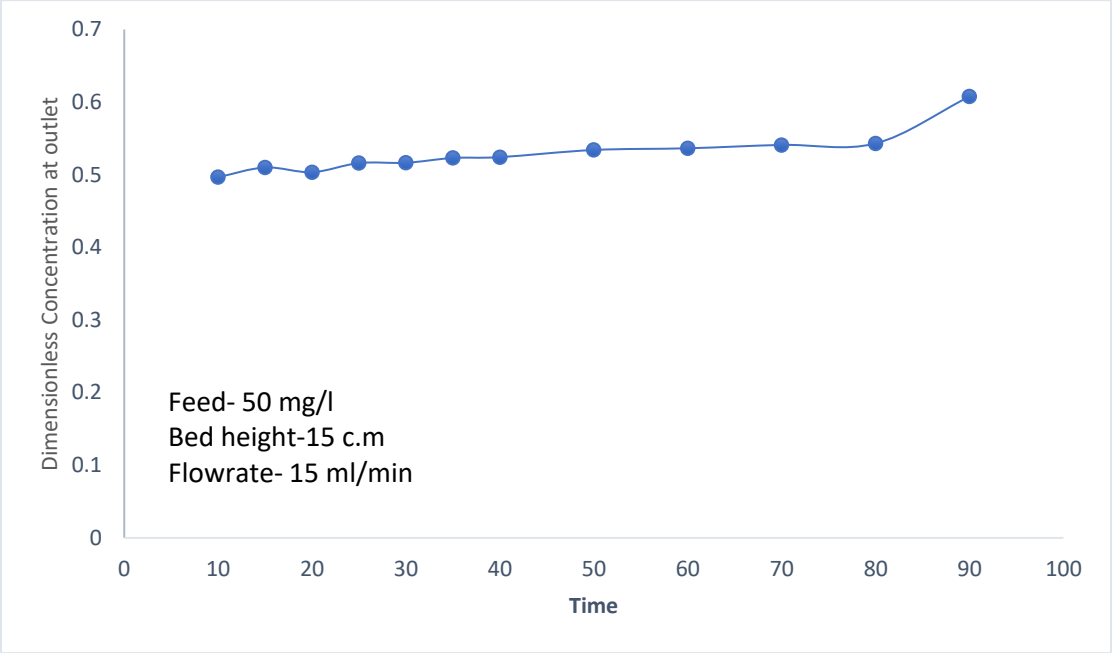


Fig.7.4.a- Effect of concentration

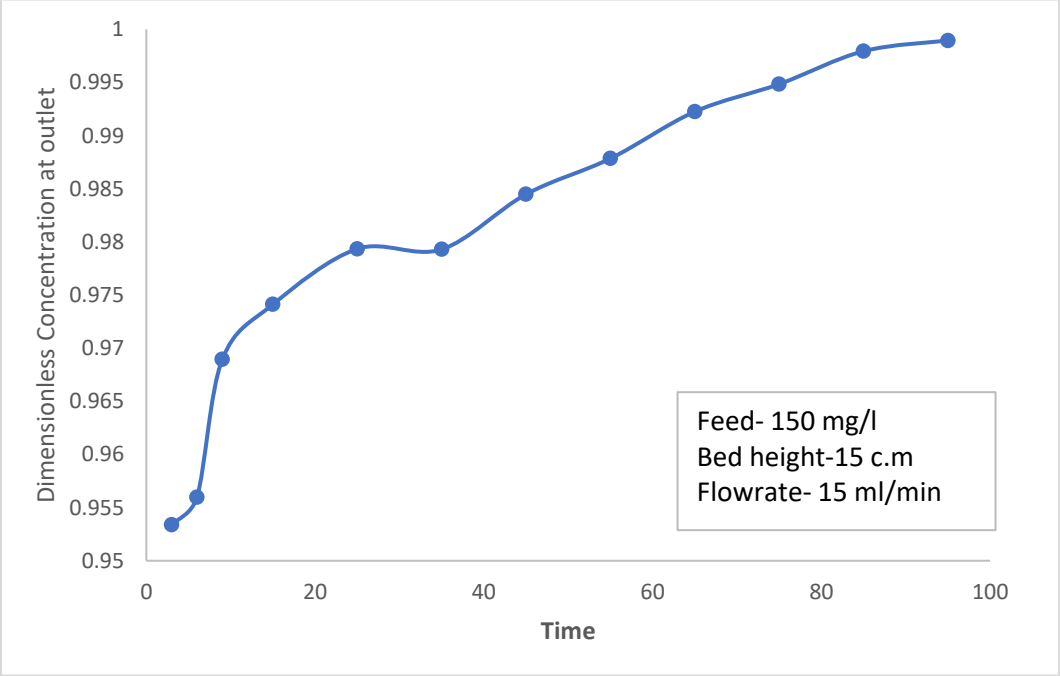


Fig.7.4.b- Effect of concentration

C H A P T E R -8

CONCLUSIONS

In this study, continuous adsorption studies were carried fixed bed using raw tamarind seed shell to remove hexavalent chromium by varying pH, bed height, feed concentration and feed flow rate. The experimental breakthrough curves were obtained using adsorbent particles, inert particles coated with adsorbent particles and adsorbent particles impregnated in sodium alginate beads. The results of this study showed that

- Removal efficiency is higher at lower pH, lower feed concentration, increased amount of adsorbent.
- Removal efficiency is higher when inert particles coated with adsorbent particles compared to adsorbent particles impregnated in sodium alginate beads
- Removal efficiency is initially higher adsorbent particles are used compared to them being coated on inert particles. However, in the long run, the breakthrough curves nearly converge to the same value.

REFERENCES

1. Sharma, Y. C. (2001). "Adsorption of Cr(VI) onto Wollastonite: Effect of pH", Indian Journal of Chemical Technology, 8, pp. 186.
2. Hu, Z., Lei, L., Li, Y. and Ni, Y. (2003). "Chromium adsorption on high-performance activated carbons from aqueous solution", Separation and Purification Technology, 31, pp. 13-18.
3. IS:2490 (Part I), Tolerance Limits for Industrial Effluents Discharged into Inland Surface Water, ISI, New Delhi, India, 1970.
4. Z. Song, C.J. Williams, R.G.J. Edyvean, Desalination 164 (2004) 249.
5. S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, J. Hazard. Mater. 102 (2003) 257.
6. Hafez, S. El-Mariharawy, Desalination 165 (2004) 141.
7. L. Marder, A.M. Bernardes, J.Z. Ferreira, Sep. Purif. Technol. 37 (2004) 247.
8. P. Venkateswaran, K. Palanivelu, Sep. Purif. Technol. 40 (2004) 279.
9. M. Murugananthan, G. Bhaskar Raju, S. Prabhakar, Sep. Purif. Technol. 40 (2004) 69. [8] Z. Hu, L. Lei, Y. Li, Y. Ni, Sep. Purif. Technol. 31 (2003) 13
10. Li J., Li Q, Zhang X., Yan Y. 2009. Kinetics parameters and mechanisms of the batch biosorption of Cr(VI) and Cr(III) onto Leersia hexandra Swartz biomass. J. Colloid Interf. Sci. 333, 71-77.
11. Beverskog B., Puigdomenech 1. 1997. Revised Pourbaix diagrams for Chomium at 25-300°C. Corrosion Sci. 39 (1), 43-57.
12. Owlad M., Aroua M. K., Daud W. A.W., Baroutian S. 2009. Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review. Water Air Soil Pollut. 200, 59-77.
13. Ma H.L., Tanner P. A. 2008. Speciated isotope dilution analysis of Cr(III) and Cr(VI) in water by ICP-DRC-MS, Talanta 77,189-194.
14. Oze C., Fendorf S., Bird D. K., Coleman R. G. 2004. Chromium geochemistry in serpentinized ultramafic rocks and serpentin esoils from the Franciscan Complex of California. Am. J. Sci. 304, 67-101.
15. McBride M. B. Environmental Chemistry of Soils, Oxford University Press: New York, 1994.
16. Fendorf S. E., 1995. Surface reactions of chromium in soils. Geoderma, 67, 55-71.
17. Das S. K., Mukherjee M., Guha A. K. 2008. Interaction of chromium with resistant Stain Aspergillus versicolor: Investigation with Atomic Force Microscopy and other physical studies, Langmuir, 24, 8643-8650,
18. Mohan D., Pittman C.U. 2006. Activated carbons and low cost adsorbents for re-mediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2), 762-811.
19. Tiravanti G., Petruzzelli D., Passino R. 1997. Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery. Water Sci. Technol. 36, 197-207.
20. Rengaraj S., Yeon K.-H., Moon S.-H. 2001. Removal of chromium from water and wastewater by ion exchange resins. J. Hazard. Mater. 87 (1-3), 273-287.

21. Rengaraj S., Yeon K.-H., Kang S.-Y., Lee J.-U., Kim K.-W., Moon S.-H. 2002. Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. J. Hazard. Mater. 92 (2), 185-198.
22. Rengaraj S., Joo C.K., Kim Y., Yi J. 2003. Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. J. Hazard. Mater. 102 (2/3), 257-275.
23. Petruzzelli D., Passino R., Tiravanti G. 1995. Ion exchange process for chromium removal and recovery from tannery wastes. Ind. Eng. Chem. Res. 34, 2612-2617.
24. Kozlowski C.A., Walkowiak W. 2002. Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes. Wat. Res. 36, 4870- 4876.
25. Shaalan H., Sorour M., Tewfik S. 2001. Simulation and optimization of a membrane system for chromium recovery from tanning wastes. Desalination. 14,315-324.
26. Ozaki H., Sharma K., Saktaywin W. 2002. Performance of an ultra-low pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters. Desalination. 144, 287-294,
27. Chauhan D., Sankararamakrishnan N. 2011. Modeling and evaluation on removal of hexavalent chromium from aqueous systems using fixed bed column. J. Hazard. Mater. 185, 55-62.
28. Loukidou M. X., Zouboulis A. I., Karapantsios T. D., Matis K. A. 2004.
29. Equilibrium and kinetic modeling of chromium(VI) biosorption by Aeromonas caviae. Colloid Surface A. 242, 93-104.
30. S. Hao, Y. Zhong, F. Pepe, and W. Zhu, “Adsorption of Pb 2+ and Cu 2+ on anionic surfactant-templated aminofunctionalized mesoporous silicas,” Chem. Eng. J., vol. 189– 190, pp. 160–167, 2012, doi: 10.1016/j.cej.2012.02.047
31. S. Singh, K. L. Wasewar, and S. K. Kansal, Low-cost adsorbents for removal of inorganic impurities from wastewater. INC, 2020.
32. M. Manyangadze, N. H. M. Chikuruwo, T. B. Narsaiah, C. S. Chakra, M. Radhakumari, and G. Danha, “Enhancing adsorption capacity of nano-adsorbents via surface modification: A review,” South African J. Chem. Eng., vol. 31, no. May 2019, pp. 25–32, 2020, doi: 10.1016/j.sajce.2019.11.003.
33. N. B. Singh, G. Nagpal, S. Agrawal, and Rachna, “Water purification by using Adsorbents: A Review,” Environ. Technol. Innov., vol. 11, pp. 187–240, 2018, doi: 10.1016/j.eti.2018.05.006.
34. M. Sulyman, J. Namiesnik, and A. Gierak, “Low-cost adsorbents derived from agricultural by-products/wastes forenhancing contaminant uptakes from wastewater: A review,” Polish J. Environ. Stud., vol. 26, no. 2, pp. 479–510, 2017, doi: 10.15244/pjoes/66769.
35. L. Joseph, B. M. Jun, J. R. V. Flora, C. M. Park, and Y. Yoon, “Removal of heavy metals from water sources in the developing world using low-cost materials: A review,” Chemosphere, vol. 229, pp. 142–159, 2019, doi: 10.1016/j.chemosphere.2019.04.198.
36. F. B. Liang, Y. L. Song, C. P. Huang, J. Zhang, and B. H. Chen, “Adsorption of hexavalent chromium on a lignin-based resin: Equilibrium, thermodynamics, and kinetics,” J. Environ. Chem. Eng., vol. 1, no. 4, pp. 1301–1308, 2013, doi: 10.1016/j.jece.2013.09.025.

37. B. H. Hameed and A. A. Rahman, “Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material,” J. Hazard. Mater., vol. 160, no. 2–3, pp. 576–581, 2008, doi: 10.1016/j.jhazmat.2008.03.028.
38. N. K. Mondal, A. Samanta, S. Chakraborty, and W. A. Shaikh, “Enhanced chromium(VI) removal using banana peel dust: isotherms, kinetics and thermodynamics study,” Sustain. Water Resour. Manag., vol. 4, no. 3, pp. 489–497, 2018, doi: 10.1007/s40899-017-0130-7.
39. C. P. Dwivedi, J. N. Sahu, C. R. Mohanty, B. R. Mohan, and B. C. Meikap, “Column performance of granular activated carbon packed bed for Pb(II) removal,” J. Hazard. Mater., vol. 156, no. 1–3, pp. 596–603, 2008, doi: 10.1016/j.jhazmat.2007.12.097.
40. H. N. Abdul Halim and K. L. K. Mee, “Adsorption of Basic Red 46 by Granular Activated Carbon in a Fixed- bed Column,” Int. Conf. Environ. Ind. Innov., vol. 12, pp. 263– 267, 2011.
41. V. M. Bhandari and V. V. Ranade, Advanced Physicochemical Methods of Treatment for Industrial Wastewaters. Elsevier Ltd., 2014.
    A. Karau, C. Benken, J. Tho¨ mmes, M.-R. Kula, The Influence of Particle Size Distribution and Operating Conditions on the Adsorption Performance in Fluidized Beds, November 1996.
42. S. Nikam & D. Mandal, A study on fluidization of activated carbon particles in gas-solid fluidized bed, August 2020,
43. Ramesh Timsina, Rajan K. Thapa, Britt M. E. Moldestad & Marianne S. Eikeland, Effect of particle size on flow behavior in fluidized beds, December 2019.
44. Z. M. Badruddoza, Z. B. Z. Shawon, M. T. Rahman, K. W. Hao, K. Hidajat, and M. S. Uddin, “Ionically modified magnetic nanomaterials for arsenic and chromium removal from water,” Chem. Eng. J., vol. 225, pp. 607–615, 2013, doi: 10.1016/j.cej.2013.03.114.