SEQUENTIAL BATCH CONTACTORS FOR REMOVAL OF CHROMIUM(VI) FROM WASTEWATER USING SHEEP’S WOOL

by

Priyasha Ray

A Thesis presented to the Faculty of the American University of Sharjah College of Engineering In Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemical Engineering

Sharjah, United Arab Emirates

May 2017
Approval Signatures

We, the undersigned, approve the Master’s Thesis of Priyasha Ray.

Thesis Title: Sequential batch contactors for removal of chromium(VI) from wastewater using sheep’s wool.

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Acknowledgment

Firstly, I would like to express my heart felt gratitude towards my advisors Dr. Taleb Ibrahim and Dr. Mustafa Khamis for their guidance, and support throughout my research work. Their continuous effort and encouragement has enabled in the systematic execution of my research work.

I am thankful to Mr. Ziad Sara for initially assisting me in the experimental work, calculations and operation of the equipment. I am indebted to him for putting in extra hours so that I would quickly get accustomed to research work.

I would like to recognize and appreciate the efforts of my colleague, Mr. Muhammad Ashraf Sabri who immensely helped me with the conceptualization of my experiments and laboratory work.

I would like to extend my gratitude towards the Department of Chemical Engineering, American University of Sharjah for empowering me with knowledge and opportunities in the scientific domain as well as supporting me with graduate teaching assistantship.

Lastly, I would like to thank my sister Pearl, for being my source of strength, inspiration and encouragement.
Abstract

The effluent streams of various industries contain heavy metals like chromium. The hexavalent form of it is highly toxic, which needs specific intensive treatment before disposal. Sheep’s wool, as a keratinous adsorbent, has been found to be able to reduce the chromium concentration below the permissible limits thus eliminating the requirement for any further treatment before disposal. In this work, sheep’s wool was used to treat synthetic wastewater containing hexavalent chromium in sequential batch contactors. The optimum parameters of dosage, time, pH, shaking speed and temperature were established by batch studies to be 8 g/L, 25 min, 2, 150 rpm and 25°C respectively. Sequential batch contactors ensured complete removal of hexavalent chromium. With three sequential batch contactors, the Cr(VI) concentration was reduced from 100 mg/L to 0.06 mg/L, which is less than the permissible discharge limit for Cr(VI) in water bodies. Desorption studies were carried out to determine the optimum parameters for effective desorption using potassium chloride. The optimum parameters in terms of time, concentration and temperature were concluded to be 25 minutes, 1.0 M and 50 °C. The removal efficiency of Cr(VI) after the third cycle was determined to be 82 ± 2 percent which is similar to the removal efficiency of Cr(VI) in the first cycle that is 83 ± 2 percent. The adsorption-desorption cycles dictate that wool can be regenerated several times without any pronounced change in its removal efficiency. The lab scale experiments were performed for 100 mL and then were scaled to 1000 mL of sample laboratory synthesized chromium wastewater. The experimental results obtained from the scale up experiment are comparable to the results obtained from 100 mL of sample laboratory synthesized solution without any significant change in removal efficiency of Cr(VI) and total chromium. Thus, this method has the potential to be scaled up to pilot plant, and eventually, industrial scale utilization for chromium removal from industrial wastewater streams.

Search Terms: hexavalent chromium, wool, sequential batch contactors, adsorption desorption cycles.
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Chapter 1: Introduction

1.1. Overview

Heavy metals are metallic elements from the periodic table that possess an atomic density greater than 6g/cm$^3$. Heavy metals are the most persistent pollutants present in wastewater and are often referred to as trace elements. The most common types of metals found in wastewater are lead, mercury, silver, arsenic, copper, cadmium and chromium. Heavy metal wastewater pollution may be caused due to natural or anthropogenic sources. Soil erosion, urban run offs, volcanic activities and aerosol particulates are natural sources of heavy metal wastewater pollution, while the discharge from mining extraction, textile industries, nuclear plants, metal finishing and electroplating industries are the anthropogenic sources of heavy metal wastewater pollution. The discharge of the heavy metals into water bodies may create serious environmental and health problems. The accumulation of heavy metals in aquatic systems greatly depress the number of living organisms. The growth of aquatic microorganisms is adversely affected causing serious setbacks in biological wastewater treatment plants. The manifestation of heavy metal pollutants takes place in plants growing on heavy metal contaminated soil, which are further consumed by animals and humans, leading to their entry in the food chain through bioaccumulation and biomagnification causing severe detrimental effects. Heavy metal polluted wastewater may prove to be fatal to humans, being toxic (acute, sub-chronic or chronic), carcinogenic, mutagenic, teratogenic and neurotoxic. For instance, wastewater contaminated with copper may lead to liver and kidney damage, vomiting, headaches, abdominal pain and the development of anemia. Exposure to water containing mercury may lead to brain disorders, gastrointestinal disorders, congenital malformation, stomatitis and gingivitis. Chromium containing wastewater may lead to brain damage, chrome ulcers, lung cancer, nasal septum perforation kidney and liver damage [1].

Hence, it becomes essential to treat heavy metal wastewater pollution owing to its environmental impact and toxicity on human health. Conventional techniques for treating heavy metal pollution include chemical precipitation, membrane filtration and ion exchange. However, these techniques have certain drawbacks such as high energy requirements, incomplete removal of heavy metals and production of toxic sludge. For instance, chemical precipitation leads to large volumes of sludge generation, where
extra operating cost are incurred for its disposal. Fouling can occur in case of membrane filtration, increasing operating costs for its maintenance and replacement. The disadvantages from conventional techniques of heavy metal wastewater pollution treatment can be overcome through adsorption. Adsorption is a popular low cost technique where the metal binding capacity of adsorbents may be utilized for the removal of heavy metals present in low concentrations in wastewater [2].

1.2. Thesis Objectives

Hexavalent chromium is a toxic compound; its accumulation in water bodies can become a serious threat to the ecosystem and adversely affect human health. Hence, hexavalent chromium must be brought down to the regulatory limit before being discharged into river bodies. The objective of the research work is to remove hexavalent chromium by employing sequential batch contactors (SBC) using Sheep’s wool as an adsorbent. Hexavalent chromium gets adsorbed on the surface of wool and is reduced to its trivalent form on its surface. Wool proves to be an effective, low cost method for heavy metal pollution treatment over conventional methods. Furthermore, the effectiveness of the adsorbent of wool will be tested over a number of adsorption-desorption cycles.

1.3. Research Contribution

Prior research work had been performed by Jumean et al. [3] where sheep’s wool was used as a low cost adsorbent for removal of hexavalent chromium in both short term and long term equilibrium batch modes. Experimental parameters optimized in their work were utilized in this thesis work. The research contribution to this work include

- Synthetic wastewater containing hexavalent chromium being treated by Sequential batch contactors to ensure complete removal of hexavalent chromium.
- Optimal parameters required to perform desorption of chromium laden wool sample such as effect of time, temperature and concentration.
- Simultaneous adsorption-desorption cycles carried out to comprehend the effectiveness of the adsorbent over a number of cycles.
1.4. Thesis Organization

The chapters of the thesis are organized as follows: Chapter 2 comprises of literature review of the various techniques that employed for the removal of hexavalent chromium from wastewater, the different types of adsorbents utilized and the different reactor configurations utilized for the removal of hexavalent chromium. Chapter 3 describes the methodology and experimental setup. The results and discussions are explained in Chapter 4. Finally, Chapter 5 summaries the thesis work and provides recommendations for future work.
Chapter 2: Literature Review

Chromium is a heavy metal, possessing oxidation states ranging from +2 to +6. Chromium compounds find application in a number of different industries as depicted in Table 1. Chromium ores are used in the production of alloys. One such alloy is Stainless steel which contains Fe, Cr and Ni in varying proportions. Chromium can be highly polished and is resistant to attacks by continuous oxidation. Hence, finds application in the production of corrosion resistant alloys. It can also be applied as a corrosion resistant decorative plating agent. The textile industries utilize chromate compounds as mordant. The leather production industry utilizes ammonium dichromate as a tanning agent. Cr(VI) compounds are found in chrome plating, inks, paints, pigments, fungicides, wood preservatives and leather tanning [4].

Table 1: Hexavalent Chromium chemicals utilized by different industries [4].

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<tr>
<th>Industry</th>
<th>Types of Hexavalent Chromium Chemicals</th>
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<tr>
<td>Anti-Corrosion Coatings (Chrome Painting, Spray Coatings)</td>
<td>Chromic Trioxide (cromic acid), zinc chromate (ZnCrO₄), barium chromate (BaCrO₄), calcium chromate, sodium chromate, strontium chromate.</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>Hexavalent chromium (when cast, welded or torch cut), ammonium dichromate(NH₄Cr₂O₇), potassium chromate, sodium chromate</td>
</tr>
<tr>
<td>Pigments in Paints, Inks, Plastics</td>
<td>Lead chromate(PbCrO₄), zinc chromate(ZnCrO₄), barium chromate, potassium chromate, sodium chromate</td>
</tr>
<tr>
<td>Wood preservation</td>
<td>Chromium trioxide</td>
</tr>
<tr>
<td>Leather tanning</td>
<td>Ammonium dichromate</td>
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</table>

In aqueous system, usually the trivalent and hexavalent forms of chromium that are predominant. The hexavalent form of chromium is toxic and a known carcinogen. It is a potential soil, surface and groundwater contaminant. The trivalent reduced form
of chromium is less toxic and is a micronutrient for humans. The solubility and aqueous speciation of chromium can be obtained from graph of the redox potential versus pH conditions, as depicted in the Figure 1. In aqueous system, trivalent chromium could occur in one of the forms as listed:

- At low pH as a cation (Cr\(^{3+}\), CrOH\(^{+2}\) or Cr (OH)\(_2\)).
- At moderate pH as insoluble hydroxide (Cr (OH)\(_3\)).
- At high pH as an anionic hydroxide Cr (OH)\(_4^{-}\)).

In aqueous system, hexavalent chromium could occur in one of the forms as listed below:

- Below pH 6.5 as monovalent (HCrO\(_4^{+}\))
- Between pH 6.5 to 10 as divalent (CrO\(_4^{2-}\)).

If the wastewater contains negligible or very little amounts of oxygen, Cr (III) become the dominant species. Conversely, in highly oxygenated drinking water or when there is a presence of strong oxidants such as chlorine or even moderately strong oxidants such as chloramine, in this case Cr(VI) become the dominant species [5].

![Figure 1: The pE versus pH diagram depicting chromium speciation [1].](image)

Hexavalent chromium has detrimental effects on human health. Hexavalent chromium enters the human body by lungs, ingestion and inhalation or through direct contact with skin. When in contact with skin Cr(VI) can cause skin irritations. On entering the body, it gets reduced to Cr(III) and binds with protein triggering
immunological response. The World Health Organization and the United States Environmental Protection Agency have declared Cr(VI) to be a toxic and regarded it to be a human carcinogen based on epidemiologic investigations of workers and of experimental studies with animals. There is a risk of getting lung cancer due to chronic inhalation of Cr(VI) compounds. Hexavalent chromium is also a genotoxic causing a wide variety of effects on the cell including counting DNA damage, gene mutation, cell transformation and dominant lethal mutations [4]. The admissible limit for effluent discharge of Cr (VI) to sewage system is 0.5 mg/L and to drinking water is 0.1 mg/L [6].

2.1. Methods for hexavalent chromium removal

The discharge of hexavalent chromium into the environment can result in damage to the ecosystem and adversely affect human health. Hexavalent chromium containing wastewater needs to be treated before being discharge into river bodies. It is crucial to follow the regulatory discharge limits prior to discharge of wastewater into river bodies. A number of physical as well as chemical processes were employed to ensure complete and efficient removal of hexavalent chromium. The methods are illustrated in this chapter.

2.1.1. Coagulation and flocculation. The quality of wastewater can be improved by three processes namely Coagulation, Flocculation and Sedimentation. Heavy metals like chromium present in tannery wastewater were removed by combining all the three processes. Coagulation is a process, where a chemical termed as coagulant is added to the water to neutralize the charge on the colloidal particles present in raw wastewater. The small particles produced during coagulation accumulate to form larger particles floc in a process called as Flocculation. The floc particles formed can be separated either by sedimentation, filtration or clarification. For instance, the addition of alum to wastewater results in the formation of insoluble gelatinous floc of Al(OH)₃, which slowly falls in water and sweeps suspended material from wastewater. The floc formation reaction is given by Equation 1 [7].

\[ \text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O} + 3\text{Ca(HCO}_3\text{)}_2 \rightarrow 3\text{CaSO}_4 + 2\text{Al(OH)}_3 + 6\text{CO}_2 + 18\text{H}_2\text{O} \quad (1) \]

Various substances like ferric chloride [FeCl₃.6H₂O], ferric sulfate [Fe₂(SO₄)₃], ferrous sulfate [FeSO₄.7H₂O], alum [Al₂(SO₄)₃.18H₂O] and lime [Ca(OH)₂] have been
utilized as coagulant and flocculant aids. Tannery wastewater containing chromium were treated using immobilized chemical coagulants [7].

2.1.2. Chemical precipitation. Chemical precipitation is a technique frequently employed in wastewater treatment plants for removal of heavy metals owing to its simplicity, effectiveness and low cost of operation. This method is usually used to treat effluent wastewater that contain high concentration of chromium of 1000 mg/L or above. The removal of Cr (VI) by chemical precipitation is a two-step process that comprises of the reduction of hexavalent chromium Cr (VI) under acidic conditions (mostly pH 2 to 3) followed by the precipitation of trivalent chromium Cr(III) as hydroxyl species. Sodium sulfite, sodium metabisulphite, ferrous sulphate, barium sulphite are commonly used reagents in chemical precipitation [8]. The removal of heavy metal from wastewater by chemical precipitation represented by Equation 2.

\[
M^{2+} + 2OH^- \leftrightarrow M(OH)_2
\]

(2)

M\(^{2+}\) and OH\(^-\) are the dissolved metal ions and the precipitant, respectively, whereas M(OH)\(_2\) is the insoluble metal hydroxide[9]. Types of chemical precipitation include:

2.1.2.1. Hydroxide precipitation. Chemicals like lime and limestone are the commonly used precipitant agents due to the low cost and availability. Lime is preferably used to treat influent wastewater with metal concentration higher than 1000 mg/L. The addition of slaked lime Ca(OH)\(_2\) resulted in maximum precipitation of Cr (III) at pH 8.7 and the concentration of chromate was reduced to 30 mg/L. Lime precipitation is enhanced by seeding the precipitant with fly ash. The fly ash-lime-carbonation treatment improved the efficiency of heavy metal removal by increasing the particle size of the precipitate. Disadvantages of hydroxide precipitation include generation of large volumes of relatively low density sludge, that can inhibit dewatering and disposal of sludge. Certain metal hydroxides generated may be amphoteric, this could create problems when there are other metals mixed in the wastewater since the ideal pH chosen for one metal might put the other metal back into the solution [8].

2.1.2.2. Sulphide precipitation. Sulphide precipitation offers more advantages over hydroxide precipitation as the solubility of metal sulphide precipitates is significantly lower than hydroxide precipitates. Besides, sulphide precipitates formed are not amphoteric. Another advantage of sulphide precipitation include the
precipitation of metals taking place in presence of chelating agents with most metals removed to extremely low concentrations at a single pH. However, drawbacks of this process include the evolution of hydrogen sulphide gas and the concern for sulphide toxicity. Though, this can be avoided by preventing sulfide reagent overdose. Currently, hydroxide and sulfide precipitation are carried out together for optimal metal removal. One such configuration is a two-stage process in which hydroxide precipitation proceeds sulfide precipitation. Each stage is proceeded by a separate solids removal step. This results in production of high quality effluent of the sulfide precipitation process as well as considerably reduced volume of sludge generated and the consumption of sulfide reagent [8].

2.1.3. Evaporation. Evaporation is used for recovery of chromium salts from rinsewater in metal finishing processes. The rinsewater after removal of metal salts, can be further reused in plating bath [10]. Two common types of Evaporators used are as follows.

2.1.3.1. Atmospheric evaporators. Dragouts from nickel and hexavalent chromium operations, can be recovered by use of Atmospheric Evaporators [11]. Atmospheric evaporation can be achieved by boiling the liquid wastewater at atmospheric conditions[10]. In an Atmospheric evaporator, water is stripped from the process solution by means of an air stream. The air stream are humidified and then released into the atmosphere. The air-to-water evaporation surface was increased by stuffing the evaporation chamber with packing material. To achieve satisfactory evaporation, heating the process solution and/or the air stream may be required. A recovery of 99.9 % can be achieved for a dragout of 1 L/hr. in four counterflowing rinses [12].

2.1.3.2. Vacuum evaporators. In vacuum evaporators, evaporation is carried out at low pressure to facilitate the boiling of liquid at reduced temperature. Vacuum condition is maintained by removing non condensable gases (air) by means of a vacuum pump [10]. The distillate recovered from vacuum evaporators is high-quality rinse water and the concentrate is process chemicals that can be further return to the appropriate process bath [12]. Single or multiple effect systems may employed to carry out vacuum evaporation of chrome plating baths. The different varieties of vacuum
evaporation equipment include climbing film, submerged tube and flash evaporators [10].

2.1.4. Solvent extraction. Solvent extraction is a separation method, where compounds are separated owing to their relative solubility in two different immiscible liquids [13]. This has become a popular wastewater treatment technique owing to the ease of operation and applicability of the technique for removal of both trace and macro amounts of metal ions. Advantages of this technique include minimum phase adsorption at boundaries and attainment of rapid equilibrium. Solvent extraction when coupled with a suitable analytical method employed for the determination of metal ions, is of importance due to the ease of control of the volume of the aqueous and the organic phases [14]. Agarwal et al. [15] used cyanex 923 as an extractant for the extraction and recovery of Cr (VI) from electroplating wastewater. This extractant was used under highly acidic conditions, pH of around 0.5, carried out in chloride medium. The reaction is very fast and time taken for extraction is only 2 minutes. The extractant can be used for a wastewater containing Cr (VI) concentration varying from 54 to 1100 ppm [15].

2.1.5. Foam fractionation. Foam fractionation is based on the principle of absorptive bubble separation, which can be applied to remove very small concentration of metal ions from aqueous solution. During this process excess of surfactant is added to the water causing gas bubbles to move upwards through the column to generate foam. This froth sustainably detaches from the liquid bulk. After the foam collapses, the concentrated liquid containing the surface active solute can be collected. The concentration and elimination of dissolved materials, comprising of surface active and non-surface active solutes from aqueous solutions can be done using this method. Foam fractionation can be operated by simple method (batch wise or continuous), and complex method that involves enriching and/or stripping. Foam fractionation column may be designed as a single stage or multistage. A number of parameters effect the solute removal efficiency, such as the gas flow rate, temperature, added electrolyte, the surfactant concentration in feed, sparger porosity, the height of the foam–liquid interface, the bubble diameter, and the solute concentration in feed technique. Some of the advantages of this method include over traditional separation processes, include easy handling, easy design, operation and scale-up, small space and energy requirements, low capital investment and operating cost [16]. De-jin et al. [17] performed an experimental study on separation of chromium containing wastewater by
continuous foam separation. The method was used to treat 20 mg/L of chromium wastewater. The optimum parameters obtained include 400 mL/min gas flux, 7.5 mL/min charge in flux, pH of 6.5, 50 cm of charge in height and 60 mg/L of surface active agent Fe(NO₃)₂[17].

2.1.6. Electrochemical treatment. Electrochemical processes have become an attractive alternative for treatment of hexavalent chromium from wastewater, in contrast to traditional methods owing to low sludge generation during the process. Hexavalent chromium was reduced to trivalent chromium, from wastewaters by using, different types of reactors such as mixed-flow reactors, mixed-flow reactors in series, plug-flow reactors and solid electrodes batch reactors [13]. Some of the disadvantages of this method are the large capital investment and the expensive operating cost of electricity supply, hence they are not widely used. Most commonly used electrolytes for the removal of hexavalent chromium from wastewater include carbon aerogel electrodes, iron rotary, aluminum electrodes, iron electrodes, stainless steel electrodes, electrochemical precipitation units having six plates and titanium electrodes. The optimum parameters along with the removal efficiency of these electrolytes have been summarized by Madhavi et al. [8]. A sub category of electrochemical method is electrocoagulation. Though, Chemical coagulation is an effective technique for treating wastewater containing heavy metals, secondary pollution caused due to the addition of coagulants, like aluminum or iron salts or organic polyelectrolytes used for the removal of colloidal matter as gelatinous hydroxides. This technique of treatment is not preferable due to production of large amount of sludge. Electrocoagulation was explored for wastewater treatment, where no chemical compounds are added as coagulating agents, instead they are generated during the electrolysis process followed by electrodissolution of a sacrificial anode which is composed of aluminum or iron. The factors that affect the electrocoagulation process are applied current density, COD, initial metal ion concentration, initial pH, COD and duration for which electroprocessing was carried out. Dermentzis et al. [6] used iron electrodes for performing electrocoagulation on industrial electroplating wastewater containing hexavalent chromium. Industrial chromium containing wastewater of initial concentration of 517 mg/L was reduced under permissible limit using current density 40 mA/cm² within 50 minutes. In contrast to chemical coagulation, Electrocoagulation
is faster, economical, reliable and efficient method of heavy metals, such as chromium and COD from water and industrial wastewater [6].

2.1.7. Electrodialysis. Formerly, Electrodialysis was utilized in desalination of saline solution, however it is gaining prominence in the treatment of industrial effluent. It is an electromembrane technique that is gaining popularity over conventional wastewater methods, due to its modularity and ability to treat pollution at the source within the process [18]. The membranes are made from thin sheets of plastic and possess either anionic or cationic characteristics. During the process, electrical potential is applied on an ion exchange membrane, resulting in the selective migration of ionized species. The ionic species present in the solution on crossing through cell compartments, the anions drift towards the anode and the cation drift towards the cathode [2]. A number of parameters, such as, its charge, mobility, relative concentrations, and applied voltage determine the rate and transport direction for each ion. The ionic separation taking place during the process can be correlated to the characteristics of the ion exchange membrane, mainly the permselectivity of it. The major advantages of electrodialysis is that separation accomplished without changing the physical state or using chemical products. Moura et al. [18] applied electrodialysis on three membranes, Nafion 450, synthetically produced MTS and MCS, then passed tannery influent wastewater through them. The percent extraction of chromium through membranes were reported to be 95% for MTS, 96% for MCS and 100% for Nafion 450 [18].

2.1.8. Cementation. Cementation is a process by which an ionized metal can be recovered. A simultaneous metal-displacement process occurs when the solution containing the dissolved metallic ions brought in contact with a more active metal such as iron. This results in a spontaneous electrochemical reduction of metal to elemental state and oxidation of sacrificial metal (iron) takes place. Cementation process is driven by the difference in electrode potentials of the metal to be recovered and the active metal. For instance, hexavalent chromium in wastewater is reduced to trivalent form when brought in contact with either elemental iron or ferrous iron. Cementation reaction are given by Equation 3 and Equation 4.

\[ 2Cr^{+6} + 3Fe^0 \rightarrow 2Cr^{+3} + 3Fe^{+3} \] \hspace{1cm} (3)

\[ Cr^{+6} + 3Fe^{+2} \rightarrow Cr^{+3} + 3Fe^{+3} \] \hspace{1cm} (4)
Cementation process is a preferable method for removing heavy metals as the process includes low energy utilization, the control requirements are simple and valuable high purity metals can be recovered [19].

2.1.9. Ion exchange. Ion exchange through synthetic resins is a popular method for removing toxic metal contaminants. Synthetic resins are commonly preferred in ion-exchange processes, as they are efficient in the removal of the heavy metals from wastewater. Cation exchangers resins are strongly acidic resins with sulfonic acid groups (-SO\(_3\)H) and weakly acid resins with carboxylic acid groups (-COOH). The metal cations in wastewater can be exchanged with hydrogen ions in the sulfonic group or carboxylic group of the resin. The cation ion exchange reaction are given by Equation 5 and Equation 6, here \( M \) denotes the metal ion [20].

\[
nR - SO_3H + M^{n+} \rightarrow (R - SO_3^-)_nM^{n+} + nH^+ \quad (5)
\]

\[
nR - RCOOH + M^{n+} \rightarrow (R - COO^-)_nM^{n+} + nH^+ \quad (6)
\]

Removal chromates from water at acidic pH values, is carried out by use of weak-base anion exchange resins. And removal of traces of chromate from tap water at neutral pH carried out by use strong-base anion-exchange resins. The anion exchange reaction are given by Equation 7 and Equation 8 [21].

\[
R - Cl + HCrO_4^- \rightarrow R - HCrO_4 + Cl^- \quad (7)
\]

\[
2R - Cl + CrO_4^{2-} \rightarrow R_2 - CrO_4 + 2Cl^- \quad (8)
\]

The advantages of ion exchange over chemical precipitation is the recovery of high metal value, selectivity towards specific metal removal, lesser volume of sludge production and the adherence of strict discharge specifications [22]. Cation resins IRN77 and SKN1 showed 95% removal efficiency towards hexavalent chromium containing wastewater. They demonstrated adsorption efficiencies of 35.58 mg/g and 46.34 mg/g respectively [22].

2.1.10. Membrane filtration. Membrane filtration processes are generally employed in water treatment processes, for removal of suspended solid, organic compounds as well as inorganic contaminants such as heavy metals [9]. Membrane filtration processes can be operated on batch mode for small scale plant and continuous mode in a large scale plant. A semi–permeable membrane is utilized during the process
to separate feed solution into permeate and concentrate as described by Kocurek et al. [23]. The outlet stream that passes easily through the membrane is termed as permeate and the pollutant particles form the concentrate stream. Driving forces for the membrane processes could be as a result of difference in concentration, temperature or pressure across the membrane. Depending on the size of particles that are retained in the membrane, the pressure driven membrane filtration process are classified as microfiltration for particle size greater than 0.1 μm and operating pressure less than 500 kPa, ultrafiltration for particle size between 10-100 nm and operating pressure between 500-1000 kPa, nanofiltration for particle size between 1-10 nm and operating pressure 1-4 MPa and reverse osmosis for particle size between 0.1-1 nm and operating pressure 3-10 MPa [23]. Reverse osmosis is a technique by which organic matter, common cations and anions, and heavy metals can be efficiently removed. Particles of sizes ranging from 0.1-1 nm can be separated by reverse osmosis and is a convenient method for separation of both monovalent and polyvalent metal ions[23]. Rad et al. [24] utilized a spiral wound type RO membrane model FILMTEC BW30-4040 that was made from thin film composite of polyamide for removing wastewater containing Cr(VI). The transmembrane pressure varied from 6 to 18 bar. And the feed concentration was varied from 5 to 100 mg/L. According to the variation of feed concentration and transmembrane pressure, the salt rejection and permeate flux obtained were in the range 99.51% to 99.8% and 19.17 to 58.75 L/m²min respectively. The highest water recovery of 42.47% and permeate flux 58.75 L/m²min were obtained at lowest feed concentration and highest pressure [24].

2.1.11. Photocatalysis. Photocatalysis is one of the latest technique implemented for quick and efficient elimination of environmental pollutants from dilute streams. A number of reliable continuous and low-cost light sources can be used such as Ultraviolet (UV) and Light Emitting Diodes (LEDs) are used to conduct photocatalysis. Semiconductors are illuminated, by light from these sources which contain photons that are more energetic than the bandgap of the semiconductor resulting in generation of electrons, which are capable of reducing certain metal species in water [25]. Cheng et al. [25] investigated photocatalysts like TiO₂, ZnO, NaTaO₃ and WO₃ for the removal of Cr(VI) from wastewater. They found all four photocatalysts to be efficient for the removal of Cr(VI), however the removal rates are affected by characteristics of the material, that is the surface area, conduction band minimum, band
gap as well as the property of the water matrix. For a wastewater at pH 7, the removal efficiency from high to low is of the order TiO$_2$ $\sim$ ZnO > NaTaO$_3$ > WO$_3$ [25].

2.1.12. **Freezing desalination.** Freezing Desalination is a physical wastewater treatment process used for removal of various organic and inorganic impurities [26]. There are two fundamental methods for carrying out freeze desalination they are suspension and progressive freeze crystallization. Freeze concentration is a conventional method used to purify liquid waste or liquid wastewater and is based on the principle of suspension crystallization, during this process many tiny ice crystals are formed and impurities get separated from the ice phase during formation of the ice crystals. This method is often complicated and requires large initial investment. In the progressive freeze-concentration a single ice crystal easily gets separated from the mother liquor [27]. Owing to simplicity and ease of operation progressive freeze concentration is usually a more preferable treatment method over suspension freeze crystallization. An application of this method was demonstrated by Melak et al. [26] examined the capacity of home-use refrigerators to generate fresh water free from Cr(VI) by melting ice produced from Cr(VI) containing water by freeze desalination. This method is utilized for removal of trace amounts of Cr(VI). In this experiment simulated water and deionized tap water were spiked with 5mg/L of Cr(VI). Plastic tubes of diameter of 20 mm were cast off with chromium water and then inserted upside down in plastic beaker. Partial freezing is performed for various time intervals, after which the beakers are taken out from the freezer and ice crystals were separated by rejecting the remaining water. This procedure is repeated several times till a small volume of concentrated solution remains. The surface of ice was washed with 20-25 mL of deionized water, to desorb the chromium that is weakly adsorbed on the surface of the ice. This method proves to have a good potential for removal of Cr(VI) from wastewater as removal efficiency of 97% and 85% were observed for deionized and tap water spiked with 5mg/L of Cr(VI) [26].

2.1.13. **Adsorption.** Adsorption is a surface phenomenon where contaminants are concentrated at the interface between two phases. Adsorption is of two types – physical adsorption and chemical adsorption. In physical adsorption, the ionic charged species such as CrO$_4^{2-}$ are held to charged surface by electrostatic attraction [28]. There exists van der Waals interaction between adsorbate and the adsorbent molecule [29]. There is no transfer of electrons during physical adsorption. Physisorption is an
exothermic process, where a decrease in free energy and entropy of the system is observed. During Chemisorption contaminates exchange electrons and a site specific reaction occurs. The two types of chemisorption reaction that could occur are ligand exchange–chelation or surface reduction followed by precipitation. Chelation is a process where a single ion is exchanged with multiple ligands. In case of Cr(VI) ligand exchange chelation can be with one or more ligands (usually hydroxyl groups) [28].

2.2. Types of Adsorbents

A number of different adsorbents have been used for the removal of wastewater containing hexavalent chromium. This section illustrates the different types of adsorbents that are employed in the removal of hexavalent chromium containing wastewater.

2.2.1 Activated carbon. Activated carbon that are derived from numerous sources, is one of the most investigated adsorbent for treating hexavalent chromium bearing wastewater. Its widespread use being attributed, to the presence of a variety functional groups such as carboxylic group, well-developed internal micro porosity structure and remarkably high surface area ranging from 500 to 1500 m²/g. The reduction in particle size during the production of activated carbon leads to increase of surface area. Activated carbon can be classified into four different categories, based on shape and size as Powered Activated Carbon (PAC), Granular Activated Carbon (GAC), Activated Fibrous Carbon (AFC) and Activated Carbon Clothe (ACC). Their physiochemical properties vary depending on the source of material and the extent of extraction. Owlad et al. [30] reviewed different varieties of activated carbon for removal of hexavalent chromium along with the optimal parameters required for its efficient removal.

2.2.2 Carbon nanotubes. Even though activated carbon is a good adsorbent, it has certain drawbacks such as inefficiency in removal of heavy metal ions in low concentrations of (ppb), slow attainment of adsorption equilibria owing to slow pore diffusion and difficulty in regeneration of adsorbent. Also efficiency of activated carbon decreases due to adsorption of moisture and hydrophilic substances. Hence Carbon nanotubes are being considered as some alternative adsorbents to activated carbon. Depending on the number of outer layers on the tubular structure carbon nanotubes are of two types that are single walled carbon nanotubes (SWCNTs) and
multi-walled carbon nanotubes (MWCNTs). MWCNTs are easy to synthesize, purify and less production cost is incurred therefore are preferred over SWCNTs. Carbon nanotubes are gaining acknowledgement due to their adsorption capabilities, small dimension, uniform pore distribution and large specific surface. They have superior porosity over activated carbon. Chemical modification of the nanotube may be done to enhance the adsorption of specific ions or molecules. Both functionalized and unfunctionalised MWCNTs have effectively removed Cr(VI) from water [31]. A process known as functionalization is performed on the carbon nanotubes to improve the interaction between matrix and pollutant. Functional groups are inserted on the side wall of the carbon nanotube. Chromium adsorption was carried out on functionalized MWCNT. Modification of virgin MWCNT can be done by sulphuric acid which is a source of proton and sulphur agents. For functionalization of MWCNT is immersed in 1M sulphuric acid for 12 hours. The treated MWCNT is then dried for 6 hours at 70 degrees. Adsorption efficiency of 59.44% is obtained using f-MWCNT [32].

2.2.3 Inorganic substances. Inorganic substances that are used in treating wastewater with hexavalent chromium can be classified into three major types such as Clay, Silica and Zeolites. Rosales-landeros et al. [33] reviewed various naturally occurring and chemically modified inorganic materials for adsorption of wastewater containing hexavalent chromium.

2.2.3.1. Silica. Silica (SiO₂) is one of the most abundantly occurring mineral on earth. Silica can also be modified and produced synthetically. The surface of Silica can be modified by either chemical or thermal treatment, which leads to change in chemical characteristics of silica surface. Silica compounds when functionalized with carboxylic acids, sulfonic acids and quaternary ammonium groups are efficient in the removal of heavy metals. Silica-based supported functional groups, find wide application in the field of selective separations due to their stability with both acid and solvent, excellent mechanical properties and lack of shrink/swell characteristics. Rosales-landeros et al. [33] compared the experimental conditions and adsorption capacity of natural and modified silica, that were utilized for the removal of Cr(VI) from wastewater. The adsorption capacity using Silica was found to be 5.5 mg/g and the adsorption capacity for Silica La(III) Chitosan was found to be 1.5 mg/g. Hence, they found that modified silica showed enhanced adsorption efficiency compared to unmodified silica [33].
2.2.3.2. Clay. Clay is a mineral usually found in sedimentary rocks. Chemically, clay comprises of aluminates and silicates which are bound to water molecules. Clay are excellent adsorbent materials due to properties such as high specific surface areas, chemical and mechanical stability. Clays possess the ability to adsorb cationic, anionic as well as neutral metal species. The experimental parameters used for the removal of hexavalent chromium using different varieties of clay have been reviewed by Rosales-Landeros et al. [33].

2.2.3.3. Zeolite. Zeolite are crystalline mineral that have a framework of linked silica and alumina tetrahedral but can also have elements other than Si and Al. This framework comprises of open cavities in the form of channels and cages with extra-framework cations that are usually exchangeable. These cavities are large enough to allow the passage of certain species. Significant properties of zeolites are uniform pore size, reversible hydration and ion exchange. Zeolites on modification can be used for adsorption of different metal ions from wastewater [33]. Zeolite modified with iron was used for removal of Cr(VI) from wastewater. The sorption capacity of this adsorbent is 0.3mg/g [34].

2.2.4. Bisorbents. A promising new technique for the removal of chromium from wastewater have been investigated using bisorbents. Bisorbents can classified into various categories such as bacteria, algae, yeast, fungi and agricultural products. A number of functional groups present in the biosorbent material are responsible for bisorption of hexavalent chromium. Biosorption offer more advantages over conventional treatment methods as they are inexpensive, provide high effectiveness, and produce minimum chemical and/or biological mud. The application of bisorbents for treatment of industrial water is favorable, due to their regeneration capacity and prospect of metal recovery. Saha et al. [35] reviewed a number of bisorbents for the removal of hexavalent chromium from industrial and municipal effluent

2.2.4.1. Bacteria. An alternative to conventional techniques of heavy metal removal is the application of microbial based technologies. Through bioaccumulation, soluble and particulate forms of metals especially dilute solutions are efficiently removed by microorganisms and microbial products [36]. Due to the small size of microorganisms, they possess high surface area to volume ratio and thus provide large contact interface that interact with metals from surrounding environments. The bacterial
cell contains structural polymers which provide acidic functional groups like carboxyl, phosphoryl and amino groups, which account for the reactivity of bacterial cells. Despite different surface formats between types of bacteria, they are intrinsically reactive towards dissolved metals [37]. A number of factors that influence the removal of Cr(VI) include cell density, temperature, pH, salt concentration, oxidation-reduction potential, metabolic inhibitors, electron donor, oxyanions and the presence of other heavy metals [36]. Bacillus circulans MN1 was a bacterium strain isolated from spent chrome effluent, was used for the removal of Cr(VI) under microaerophilic conditions [37]. Bacillus spp was isolated from soil was employed for the removal of low amounts of chromium from wastewater [38]. Halomonassp. VITP09 is a halophillic and halotolerant marine bacteria growing in high salt concentration, has immense potential to remove chromium [39].

2.2.4.2. Algae. Algae can be cultivated for the removal of certain metals from wastewater. They possess the ability to accumulate high concentration of metals form polluted aquatic systems. The mechanism of metal accumulation within algae involves two processes: an initial rapid (passive) uptake proceeded by a much slower (active) uptake. Physical adsorption occurs during the passive uptake, where metal ions get adsorbed over the cell surface rapidly in a few seconds or minutes. This step is metabolism independent. During chemisorption, which is metabolism dependent, where the metal ions are slowly transported across the cell membrane into the cytoplasm [40]. Blue green algae Spirulina sp. was used in the removal of Cr(VI) from aqueous effluent streams [41]. Similarly Padina boergesenli brown marine algae was utilized in the removal of Cr(VI) from electroplating effluent [42]. Immobilized Chlorella Pyrenoidosa was employed for the removal of Cr(VI) from synthetic wastewater in alginate and carrageenan matrices. Immobilization usually tends to increase the metal uptake by biomass [43].

2.2.4.3. Yeast. Yeast proves to be a promising biomass capability for removal of Cr(VI) from wastewater. Chromium uptake by yeast involve both bisorption and metabolism depending accumulations. Factors affecting bisorption depend upon microbial strain, its physiological state, growth conditions, metal speciation, cell wall composition and presence of pigments. The most crucial factors for bisorption are biomass concentration and metal speciation closely associated with solution pH. The Cr(VI) tolerance and uptake ability was tested using a variety of pigmented and non-
pigmented yeasts strains. The strains tested include *Saccharomyces cerevisiae* 1968, *Williposis californica* 248, *Candida krusei* 61t, *R. aurantiaca* 1198, *R. aurantiaca* 1195, *Rhodotorula* sp.4, pink-pigmented *Rhodotorula mucilaginosa*, and black yeast *Crytococcus* sp. *W*. The metal sorption capacity by yeasts is determined by the composition of its cell wall. The key role in the processes of sorption by pigment-less yeast is performed by chitin and glucan-mannoprotein complex. While sorption by pigmented yeasts occurs due to chelation properties of melanin and carotenoids. The development of chromium bio-remediation technologies is by combining yeasts strains of high Cr(VI)-tolerance and high Cr(VI) accumulation ability [44].

**2.2.4.4. Fungi.** Fungal organisms generally find application in a variety of industrial fermentation processes. Fungi grow rapidly to produce high yield of biomass. Fungi can be genetically and morphologically manipulated. Cr(VI) was removed from aqueous solution by *Aspergillus niger*, a fungal strain isolated from polluted air with industrial vapors [45]. Bioremediation of hexavalent chromium containing tannery waste was carried out using *Trichoderma harizianum* [46]. The removal of Cr(VI) by industrial xylanase producing strain *Aspergillus awamori* performed [47].

**2.2.4.5. Agricultural waste.** Natural bisorbents in the form of agricultural waste are present in abundance and provide a good alternative to inexpensive synthetic adsorbents. Agricultural waste comprises of polysaccharides, proteins, lignin which have associated functional groups responsible for metal ion adsorption. Metals are held to the sorbent surface either physically (London Van Der Waal Forces) or chemically by (ionic or covalent bonds), this implies that both physisorption as well chemisorption can take place on the surface of the bisorbents [48]. Agricultural waste such as okra leaves [48], eucalyptus bark [49], lemon skin [50], soya cake [51], compost from carnation flowers [52], grape stalk and yohimbe bark waste [53] were used in batch adsorption studies for the removal of hexavalent chromium. Continuous adsorption experiments were carried in fixed bed adsorption columns by bisorbents like coconut coir [54], eucalyptus bark [55], mango seed shell [56], tamarind seeds [57] and flamboyant pods [58].

**2.2.5. Industrial waste.** Industrial waste are generated as byproducts of various industries. As industrial waste are inexpensive, locally available and require very little processing and have good adsorptive capacity they can be used as low-cost adsorbent
for the removal of heavy metals from wastewater. Prior to their use for treatment of wastewater, several parameters need to be considered, such as their ability to remove a wide variety of heavy metals, adsorption capacity, maximum removal of specific metals, regeneration capacity, cost effectiveness and their tolerance towards a varied range of concentration of heavy metals and other wastewater parameters [59]. Hexavalent chromium was removed using distillery sludge as an adsorbent. The adsorbent proves to be economic and solves the problem of solid waste disposal [60]. Tea factories during tea production usually discard the woody overgrown shoots of the tea plant. This forms the tea factory waste. Tea factory waste have been used for the efficient removal of chromium [61]. Coffee Waste are solid wastes obtained from extraction process of instant coffee manufacturing and final residues generated from cafeterias. Coffee waste was used as an adsorbent for the removal of Cu(II) and Cr(VI) from synthetic wastewater [62]. Batch adsorption experiments for removal of Cr(VI) using flyash as an adsorbent, which is a waste generated from power plants [63]. Sawdust obtained from untreated rubber wood was used as an adsorbent in batch scale adsorption experiments for removal of Cr(VI). Wood sawdust is a solid waste product generated from mechanical processing. It comprises of lignin (23-30%) and cellulose (45-50%), providing sites for metal cations due to carboxylic, hydroxyl and phenolic groups present on the structure [64].

2.2.6. Keratinous material. Keratin are protein molecules, largely found in wool, horns, nails, birds feathers and human hair. Keratinous materials derived from biological sources such as sheep’s wool, human hair and poultry feathers have the immense potential to be applied as adsorbents in wastewater treatment [65]. More than five million tons per year of keratinous wastes from feathers, horns, nails and poor quality wool from sheep breeding and byproducts from textile industry are generated. These materials can be utilized as adsorbents in numerous forms such as loose-fibers, nonwovens, hybrid membranes, short fibers or particles, and colloidal solutions [66]. Keratinous adsorbents offer the prospective of regeneration and reuse after the separation of heavy metal ions. Both physisorption and chemisorption can occur on the surface of keratinous materials. In case of physisorption pollutants are trapped on the porous surface of keratin materials. For chemisorption, pollutants bind with various functional groups present on the keratin protein. Specifically, The peptide bonds and side chains of amino acid residues offer active chemical sites for metal binding [65].
2.2.6.1. Sheep’s wool as an adsorbent. Wool is generated as a keratinous waste from sheep breeding and can be used as a novel adsorbent [67]. Wool powders have been used to remove Co(II). Here, wool was used in powdered form, as its reactivity gets enhanced on conversion from fiber to powder form [68]. Waste wool obtained from woolen industries was utilized as an adsorbent for the removal of Cu(II) [69]. Electrospinning is a low cost effective technique used to extract nanofibre membrane from keratin protein of wool. Nanofibers derived from wool of mean diameter of 240 nm were tested for selectivity towards Cu(II), Ni (II) and Co(II). The results of the experiments showed selectivity of the metal ions by keratin nanofiber membrane in the following order Cu(II)> Ni(II)>Co(II) [66].

Table 2 provides the adsorption capacity of a variety of different adsorbents along with the optimal pH. Sheep’s wool was chosen for this research work. It is a type of keratinous adsorbent. In comparison to the other adsorbents from Table 2, it is observed that Sheep’s wool offers the third highest adsorption capacity after Okra leaves and Activated carbon FS-100. Sheep wool is a waste generated from slaughter houses and is readily available in comparison to Okra leaves. Activated carbon is usually more expensive compared to bisorbents and keratinous adsorbents. Hence, wool was preferred over other adsorbent for this research work. The adsorption capacity offered by wool is 64.5 mg/g. This adsorbent works best under highly acidic condition of pH 2.

Jumean et al. [3] had used sheep’s wool as an adsorbent to remove hexavalent chromium containing wastewater. They investigated the influence of parameters such as contact time, pH, and adsorbent dosage on removal efficiency. Prior to the experiment raw wool obtained from the sheep was washed using detergent and water. Then the washed wool was left to air dry. The wool was sized to give 2 cm long fibers and then placed in a sealed container labeled as “original wool”. A part of this wool was milled to produce powder below 0.60 mm (mesh 30) labeled as “powdered wool”. 100 mL of 100 ppm of acidified potassium dichromate solution was prepared in a conical flask. Both original wool and powdered wool of adsorbent dosage 8 g/L were placed into the flask. The flask was then shaken at a speed of 150 rpm at 25oC for 3 hours. Analytes were collected after every 15 minutes. The concentration of chromium was plotted with time as shown in Figure 2.
Table 2: Adsorbent for the removal of Cr(VI) with the adsorption capacity and pH.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon, FS-100</td>
<td>3</td>
<td>69.3</td>
<td>[30]</td>
</tr>
<tr>
<td>Activated carbon fabric cloth</td>
<td>2</td>
<td>22.29</td>
<td>[30]</td>
</tr>
<tr>
<td>Functionalized MWCNT</td>
<td>6</td>
<td>41.15</td>
<td>[31]</td>
</tr>
<tr>
<td>Functionalized MWCNT</td>
<td>6</td>
<td>60.97</td>
<td>[31]</td>
</tr>
<tr>
<td>Silica</td>
<td>2 -4</td>
<td>1.5</td>
<td>[33]</td>
</tr>
<tr>
<td>Silica La(III) Chitosan</td>
<td>2 – 4</td>
<td>5.5</td>
<td>[33]</td>
</tr>
<tr>
<td>Red clay</td>
<td>4 – 6</td>
<td>1.3</td>
<td>[33]</td>
</tr>
<tr>
<td>Spend Activated Red clay</td>
<td>4 – 6</td>
<td>4.3</td>
<td>[33]</td>
</tr>
<tr>
<td>Okra Leaves</td>
<td>2</td>
<td>81.94</td>
<td>[48]</td>
</tr>
<tr>
<td>Eucalyptus bark</td>
<td>2</td>
<td>45</td>
<td>[49]</td>
</tr>
<tr>
<td>Soya Cake</td>
<td>1</td>
<td>0.28</td>
<td>[51]</td>
</tr>
<tr>
<td>Carnation flowers</td>
<td>2</td>
<td>6.25</td>
<td>[52]</td>
</tr>
<tr>
<td>Tea Factory Waste</td>
<td>2</td>
<td>54.65</td>
<td>[61]</td>
</tr>
<tr>
<td>Coffee Waste</td>
<td>5</td>
<td>45</td>
<td>[62]</td>
</tr>
<tr>
<td>Sheep wool</td>
<td>2</td>
<td>64.5</td>
<td>[3]</td>
</tr>
<tr>
<td>Human hair (black)</td>
<td>1.5</td>
<td>30.78</td>
<td>[65]</td>
</tr>
<tr>
<td>Human hair (white)</td>
<td>1.5</td>
<td>27.75</td>
<td>[65]</td>
</tr>
</tbody>
</table>

The results obtained Figure 2 indicate the UV and the ICP for total Cr and Cr(VI) were identical, hence it is deduced that that Cr(VI) is the only species present in the analyte. Another observation that is made from Figure 2 is that the Original and Powder UV spectra overlap. Hence it can be inferred that the particle size does not have discernable effect on the removal efficiency of wool. They reported removal efficiency of 88% at the end of 3 hours [3].
Figure 2: Variation of total chromium and Cr(VI) concentrations with time using original and powdered wool as adsorbents in the short term mode. Adsorbent dosage = 8.0 g/L, pH = 2.0, T = 25.0°C and shaking speed = 150 rpm [3].

In order to observe the effect of pH, the experiment was performed on a long term mode of 5 days. The operating condition utilized being 100 ppm of initial chromium solution adsorbent dosage of 8 g/L, shaking speed of 150 rpm and temperature of 25°C. The synthetic wastewater was subjected to pH ranging from 1.5 to 6. Table 3 indicates the percentage removal of Cr(VI) and total chromium by original and powdered wool. The lowest percentage removal of Cr(VI) of 7.8% for original wool and 11.7% for powdered wool is observed at pH 4. Negligible amount of Cr(VI) removal is observed at pH 6. The highest removal of Cr(VI) of 92.1% for original wool and 95.8% for powdered wool is observed at pH 2. Hence, the removal efficiency of wool for Cr(VI) is favored at high acidity [3].

The effect of wool dosage was tested for 2, 8 and 16 g/L. A long term mode experiment of 5 days was conducted using 100 ppm of initial concentration of chromium acidified at pH 2, shaking speed of 150 rpm and temperature of 25°C. Figure 3 provides the effect of adsorbent dosage of wool on the removal efficiency. It was inferred that the rate of reduction of Cr(VI) to Cr(III) increases with dosage. However, at 16 g/L, the removal of total chromium was hindered. Hence, 8 g/L is was chosen as the optimal wool dosage to carry out adsorption [3].
Table 3: Percentage removal of Cr(VI) and total chromium by original and powdered wool as a function of pH in long term mode (5 days). Adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, T = 25°C, Initial concentration of chromium = 107.4 ± 1.5 ppm. Concentration in ppm [3].

<table>
<thead>
<tr>
<th></th>
<th>pH = 1.5</th>
<th></th>
<th>pH = 2</th>
<th></th>
<th>pH = 4</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Final Conc</td>
<td>% Removal</td>
<td>Final Conc</td>
<td>% Removal</td>
<td>Final Conc</td>
<td>% Removal</td>
</tr>
<tr>
<td>Total Cr</td>
<td>±0.02</td>
<td>±0.7</td>
<td>±0.03</td>
<td>±1.0</td>
<td>±1.0</td>
<td>±0.07</td>
</tr>
<tr>
<td>Original</td>
<td>24.3</td>
<td>76.7</td>
<td>7.9</td>
<td>92.1</td>
<td>94.7</td>
<td>11.8</td>
</tr>
<tr>
<td>Powdered</td>
<td>25.9</td>
<td>75.2</td>
<td>4.2</td>
<td>95.8</td>
<td>87.3</td>
<td>18.7</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>2.2</td>
<td>97.9</td>
<td>3.1</td>
<td>96.8</td>
<td>92.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Powdered</td>
<td>5.5</td>
<td>96.9</td>
<td>9.7</td>
<td>90.0</td>
<td>88.3</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Figure 3: Variation of percent removal of Cr(VI) and total chromium with adsorbent dosage in long term mode using wool as adsorbent. Initial concentration of Cr(VI) = 100 ppm, pH = 2, shaking speed = 150 rpm and T = 25°C [3].

The adsorption data were best fitted to the Langmuir model. The data fitting was done for both short term of 3 hours and long term modes of 5 days. The parameters of the Langmuir constants are presented in Table 4. Through the results obtained from the short term mode, they postulated a two-step mechanism. The first step involves a rapid adsorption process on the wool surface accompanied by rapid equilibrium. The second step involves the reduction of Cr(VI) to Cr(III), followed by release of Cr(III)
into the solution. From Table 4, it is observed that the value of $Q$ obtained is larger for Cr(VI) than total chromium in case of long term mode. For instance, at pH 2 and long term mode of 5 days the adsorption capacity of Cr(VI) is 64.9 mg/g and the adsorption capacity for total chromium is 41.8 mg/g. This indicates that more sites are available for Cr(VI) adsorption in the long term mode. This phenomenon was explained by postulating that certain sites occupied by Cr(VI) undergo simultaneous reduction and release of Cr(III) into the solution.

Table 4: Langmuir parameters ($b$, $Q$, $R^2$) for Cr(VI) and total chromium for short term and long term equilibration period, with original wool as adsorbent. Adsorbent dosage = 8.0g/L, shaking speed = 150 rpm, T = 25°C [3].

<table>
<thead>
<tr>
<th></th>
<th>Short term mode 3hrs, pH=1.5</th>
<th></th>
<th>Long term mode 5 days, pH=1.5</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b$</td>
<td>$Q$</td>
<td>$R^2$</td>
<td>$b$</td>
</tr>
<tr>
<td>Total Cr</td>
<td>0.0061</td>
<td>48.5</td>
<td>0.999</td>
<td>Nonlinear plot</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>0.0095</td>
<td>38.0</td>
<td>0.997</td>
<td>0.034</td>
</tr>
<tr>
<td>Short term mode 3hrs, pH=2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>0.047</td>
<td>48.5</td>
<td>0.994</td>
<td>0.066</td>
</tr>
<tr>
<td>Total Cr</td>
<td>0.066</td>
<td>42.0</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Long term mode 5 days, pH=2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>0.0522</td>
<td>64.9</td>
<td>0.978</td>
<td>0.0485</td>
</tr>
<tr>
<td>Total Cr</td>
<td>0.0485</td>
<td>41.8</td>
<td>0.995</td>
<td></td>
</tr>
</tbody>
</table>

The optimal parameters obtained from the short term adsorption experiment with wool include adsorbent dosage of 8 g/L, shaking speed of 150 rpm, pH 2 and contact time of 3 hours. On observation from Figure 2, it is deduced that wool was saturated with Cr(VI) by 25 minutes. Hence, for this research work we chose 25 minutes to be contact time maintained in each stage of the SBC experiment.
2.3. Sequential batch contactors for removal of hexavalent chromium

H. Roy [70] obtained a US Patent for Chromium reduction process. Acidified chrome waters are passed through a bed of non-powdery elemental iron particles. The reduction of hexavalent chromium to non-toxic trivalent state was carried out using reactors of different configurations. In the first configuration, the process was carried using a single reactor with multiple passes. In the second configuration two reactors containing beds of elemental iron particles are connected in series. Scrap iron from various manufacturing facilities such as those used in fingernail clippers, belt buckles were used in the manufacturing of the reactor. A complete reduction of hexachrome was carried out, the particle size of the bed of particulate iron is adequately large so that hexachrome and sulphuric acid can flow by gravity through the bed [70].

Bisorbent obtained from olive stone was utilized for the removal of Cr(VI) in a two stage SBC process derived from reduction of Cr(VI) under acidic conditions. Following experimental condition were chosen for the first stage: initial concentration of Cr(VI) = 10 mg/L, pH = 2, temperature = 25°C, contact time = 180 min and concentration of bisorbent = 14 g/L. On completion of the contact time, solution is filtered and analysis of chromium is carried out. Prior to transferring the solution to the second stage, pH of the supernatant is adjusted to 4, the rest of the parameters are maintained as it, except the contact time, which was taken as 90 min. The first stage resulted in 96.38% removal and reduction of Cr (VI) to Cr(III). In the second stage 31% of total chromium is removed [71].
3.1. **Chemicals and Materials**

Analytical reagent grade Potassium dichromate ($K_2Cr_2O_7$) and 1, 5 diphenyl carbizide were purchased from SD Fine Chemicals. Potassium chloride was purchased from Parachem. Acetone and hydrochloric acid were purchased from Panacea. Sheep’s wool was purchased from Sharjah animal market.

3.2. **Instrumentation**

Cary a 50 UV-Visible Spectrophotometer (Varian, Australia) was used for the analysis of hexavalent chromium. Varian Liberty axial sequential inductively coupled plasma - atomic emission spectrometer (ICP-AES, Varian, Australia) was used for the analysis of total chromium. The Wise Shaker® was used for carrying out the SBC experiment to provide the desired shaking speed of 150 rpm. The Edmund Buhler Shaker GmbH was used for carrying out the adsorption desorption cycle experiment, as it was able to provide the temperature range of 25° C to 50° C and desired shaking speed of 150 rpm.

3.3. **Calibration curve of hexavalent chromium**

To obtain the calibration curve of hexavalent chromium, the following procedure must be followed

1. Stock solution of 100 ppm of potassium dichromate ($K_2Cr_2O_7$) was prepared.
2. Standard solution of 10 ppm of hexavalent chromium was prepared by utilizing the Stock solution of 100 ppm, through appropriate dilution with distilled water.
3. Sample solution ranging 0.2 ppm to 1 ppm were prepared by withdrawing appropriate volumes from the standard solution.
4. Stock ligand solution is prepared by dissolving 250 mg of 1, 5 diphenyl carbizide in 500 mL of acetone.
5. 0.2mL of ligand and 2 drops of 6 M $H_2SO_4$ were added to the sample solution followed by dilution to 10 mL. Color development takes place when ligand solution is added to the sample solution [3].
6. The absorbance of the solutions was read on the UV Visible Spectrophotometer at a wavelength of 540 nm.
7. The graph of absorbance versus concentration in ppm were plotted, to obtain the extension index.
3.4. Sequential batch contactors (SBC)

A number of conical flasks were used to create a lab scale setup that resembled a SBC. The Wise Shaker® was used to provide the necessary agitation speed required for adsorption. The experiment was carried in short contact time mode. Four conical flasks were made to resemble a four stage SBC for complete removal of hexavalent chromium from synthetic wastewater. The schematic representation of the SBC is depicted in Figure 4. A contact time of 25 minutes is provided in each stage of the SBC. At the end of each stage, the solution was transferred to a filtration system, which is prepared by placing a funnel into a conical flask with whatman paper of appropriate size. The supernatant collected from the first stage was transferred into the second stage. Fresh adsorbent of same adsorbent dosage is added into the second stage. The second stage is subjected to the same experimental conditions as the first stage, which was maintained till the fourth stage.

![Figure 4: Schematic representation of sequential batch contactors.](image)

Prior to the experiment, cleaning of wool was done using detergent. Later it was left to dry in open air. Wool fibers were cut into 2cm length and then stored in a container. A temperature of 25 ± 2° C was maintained throughout the expanse of the experiment. The experiment is carried out using three replicates. The procedure for carrying out the experiment is as follows.
1. Stock solution of 500 ppm of potassium dichromate($K_2Cr_2O_7$) was prepared.
2. 100 mL volume of synthetic wastewater of 100 ppm potassium dichromate($K_2Cr_2O_7$) acidified solution at pH 2 was prepared in a conical flask using the prepared stock solution.
3. Wool of adsorbent dosage 8 g/L is placed into the first conical flask/stage.
4. Conical flask with the wool samples are placed into the shaker operated at a shaking speed of 150 rpm. A contact time of 25 minutes was provided.
5. At the end of each contact time the supernatant is collected using the filtration system. The pH of the supernatant is adjusted to 2, it is transferred into a second conical flask/stage.
6. Fresh adsorbent of same dosage of 8 g/L is placed into the second stage.
7. The second stage is placed into the shaker and subjected to same operating conditions. The procedure is carried out till the fourth stage.
8. Samples are collected at the end of each stage for analysis of hexavalent and total chromium.
9. The above experiment is scaled up from 100 mL to 1000 mL of acidified sample solution of potassium dichromate utilizing the same operating conditions as before, to observe the effect of scale up.

3.5. Regeneration Studies

Regeneration studies were performed to obtain the optimal parameters required for effective desorption. Desorption of chromium laden wool sample was carried out using potassium chloride. Before, proceeding with desorption the adsorbed wool samples are rinsed with distilled water. The parameters that were examined include time, temperature and concentration.

3.5.1. Effect of time. The adsorbed wool samples are now soaked in 100 mL of 0.1M KCl solution. The adsorbent dosage used was 8 g/L. The conical flask is then placed into the Edmund Buhler shaker to provide the desired shaking speed of 150 rpm and temperature of 50 °C. Samples were collected for analysis at 2, 5, 10, 15 and 25 minutes. The experiment was performed using three replicates.

3.5.2. Effect of temperature. The adsorbed wool samples are soaked in 100 mL of 0.1M KCl solution. The experimental condition required to perform the experiment were adsorbent dosage of 8 g/L, shaking speed of 150 rpm and contact time
of 25 minutes. The Edmund Buhler shaker is preset to 25 °C, 35 °C, and 50 °C prior to placing the conical flasks into the shaker. The experiment was performed using two replicates.

3.5.3. **Effect of concentration.** The adsorbed wool samples were subjected to desorption using 0.1M and 1M KCl solution. The experimental condition required to perform the experiment are: adsorbent dosage 8 g/L, shaking speed 150 rpm, temperature 50 °C and contact time of 25 minutes. The experiment was performed using two replicates.

3.6. **Adsorption-desorption cycle**

Simultaneous adsorption desorption studies were carried out, to understand the effectiveness of the same adsorbent over a number of cycles. A cycle comprises of an Adsorption step followed by a desorption step. The schematic representation of a simultaneous adsorption desorption cycle is represented in Figure 5. The Edmund Buhler Shaker was used to provide the required agitation speed and temperature required to carry out the reaction. A filtration system is used at the end of each adsorption desorption step to collect the supernatant. The filtration system is obtained by placing a funnel with whatman paper into a conical flask. Desorption of the adsorbent is carried out by using 0.1M KCl solution. The effectiveness of the adsorbent is checked for three adsorption desorption cycles.

![Figure 5: Schematic representation of simultaneous adsorption desorption cycle with initial experimental condition.](image)

3.6.1. **Adsorption step.** A temperature of 25 ± 2° C was maintained throughout expanse of the experiment. The experiment is carried out in three replicates. The procedure for carrying out the experiment is as follows.
100 mL volume of synthetic wastewater of 100 ppm of acidified potassium dichromate \((K_2Cr_2O_7)\) solution adjusted to pH 2 is prepared in a conical flask.

- Wool of adsorbent dosage 8 g/L is placed into the conical flask.
- The conical flask is then placed into the shaker and agitated at 150 rpm.
- Samples were collected at every 5-minute time interval for analysis of chromium.
- A contact time of 25 minutes is provided. The solution is then passed through a filtration system. The supernatant of the solution is thrown into a waste bottle.
- The same adsorbent is then subjected to a desorption step.
- The adsorption efficiency was calculated using Equation 7.

\[
\%\text{Removal} = \frac{c_0-c_t}{c_o} \times 100 \tag{7}
\]

where % Removal denotes the adsorption efficiency of wool towards chromium. \(c_o\) and \(c_t\) denotes the initial and equilibrium concentration of chromium in mg/L respectively [72].

### 3.6.2. Desorption step.

The temperature of Edmund Buhler Shaker is adjusted to 50 ± 2°C was maintained throughout expanse of the experiment. The experiment is carried out using three replicates. The procedure for carrying out the experiment is as follows.

- The adsorbed wool samples are rinsed with distilled water.
- 0.1M Potassium chloride KCl Solution is transferred to the wool sample (the one which already subjected to adsorption).
- The conical flask is then placed into the shaker and agitated at 150 rpm.
- A contact time of 25 minutes is provided. The solution is then passed through a filtration system.
- The same adsorbent is again subjected to an adsorption step.
- The above procedure is carried out for 3 cycles.
- The desorption efficiency was calculated using Equation 8.

\[
\text{Desorption efficiency} = \frac{\text{Amount of chromium desorbed}}{\text{Amount of chromium adsorbed}} \times 100 \tag{8}
\]

where the amount of chromium adsorbed and amount of chromium desorbed are grams of solution.
Chapter 4: Results and Discussions

4.1 Sequential batch contactors

4.1.1 Effect of contactors. Four contactors in series were used to perform the experiment. The concentration of both Cr(VI) and total chromium decreased as it passed from one stage to another. The experiments were performed for different volumes of synthetic wastewater solution. As depicted in Figure 6, A denotes 100 mL volume of synthetic wastewater solution, whereas B denotes 1000 mL volume of synthetic wastewater solution. Sample solution from the supernatant were collected at the end of each stage for analysis. The supernatant from the fourth stage after being read on the UV and the ICP, showed chromium concentration below the detection limit.

![Figure 6: Chromium concentration in different stages of SBC. Initial Cr(VI) = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0, T = 25.0°C and shaking speed = 150 rpm. SBC 1 = 0 - 25 min, SBC 2 = 25 – 50 min and SBC 3 = 50 – 75 min. Volume = A: 100 mL, B: 1000 mL of wastewater sample solution.](image)

Table 5 provides the data for concentration of chromium at the end of every stage for 100 mL volume of synthetic wastewater solution. The concentration of Cr(VI) decreased from 100 ppm to 13.66 ppm in the first stage, from 13.66 ppm to 1.55 ppm in the second stage and from 1.55 ppm to 0.06 ppm in the third stage. Similar effect was observed for total chromium where the concentration of total chromium decreased from 100 ppm to 14.74 ppm in the first stage, from 14.74 ppm to 4.64 ppm in the second stage and from 4.64 ppm to 2.41 ppm in the third stage. Table 6 provides the data for
concentration of chromium at the end of every stage for 1000 mL volume of synthetic wastewater solution. The concentration of Cr(VI) decreases from 100 ppm to 11.98 ppm in the first stage, from 11.98 ppm to 1.45 ppm in the second stage and from 1.45 ppm to 0.04 ppm in the third stage. Similar effect is observed for total chromium where the concentration of total chromium decreases from 100 ppm to 12.83 ppm in the first stage. From 12.83 ppm to 3.64 ppm in the second stage. And from 3.64 ppm to 1.39 ppm in the third stage.

Table 5: Concentration and percentage removal of chromium during each stage in SBC for 100 mL wastewater solution. Initial Cr(VI) = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0 and T = 25.0°C, shaking speed = 150 rpm. SBC 1 = 0 - 25 min, SBC 2 = 25 – 50 min, SBC 3 = 50 – 75 min.

<table>
<thead>
<tr>
<th>Chromium concentration and removal</th>
<th>No of Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration of Cr(VI) (ppm)</td>
<td>10.06 ± 0.05</td>
</tr>
<tr>
<td>Cumulative removal of Cr(VI) (%)</td>
<td>99.97 ± 0.01</td>
</tr>
<tr>
<td>Stage-wise removal of Cr(VI) (%)</td>
<td>97.52 ± 1.11</td>
</tr>
<tr>
<td>Concentration of total Cr (ppm)</td>
<td>2.41 ± 0.92</td>
</tr>
<tr>
<td>Cumulative removal of total Cr (%)</td>
<td>98.19 ± 0.69</td>
</tr>
<tr>
<td>Stage-wise removal of total Cr (%)</td>
<td>54.45 ± 15.87</td>
</tr>
</tbody>
</table>

Table 6: Concentration and percentage removal of chromium during each stage of SBC for 1000 mL wastewater solution. Initial Cr(VI) = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0 and T = 25.0°C and shaking speed = 150 rpm. SBC 1 = 0 - 25 min, SBC 2 = 25 – 50 min, SBC 3 = 50 – 75 min.

<table>
<thead>
<tr>
<th>Chromium concentration and removal</th>
<th>No of Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration of Cr(VI) (ppm)</td>
<td>11.98 ± 0.30</td>
</tr>
<tr>
<td>Cumulative removal of Cr(VI) (%)</td>
<td>99.98 ± 0.01</td>
</tr>
<tr>
<td>Stage-wise removal of Cr(VI) (%)</td>
<td>98.34 ± 0.73</td>
</tr>
<tr>
<td>Concentration of total Cr (ppm)</td>
<td>1.39 ± 0.57</td>
</tr>
<tr>
<td>Cumulative removal of total Cr (%)</td>
<td>98.75 ± 0.52</td>
</tr>
<tr>
<td>Stage-wise removal of total Cr (%)</td>
<td>66.78 ± 10.94</td>
</tr>
</tbody>
</table>
In comparison with the work produced by Jumean et al. [3] it is deduced that the SBC scheme is successful in efficiently reducing the contact time for the experiment. It eliminates the requirement of 5 days for complete removal of hexavalent chromium. Three stages with adsorbent dosage of 8 g/L are sufficient to treat 100 ppm of Cr(VI) containing wastewater and bringing it within the regulatory permissible limit.

4.1.2. Percentage removal of chromium. Figure 7 depicts the percentage removal of Cr (VI) and total chromium in the SBC. A represents batch experiment with 100 mL initial volume of synthetic wastewater solution while B represents batch experiment with 1000 mL initial volume of synthetic wastewater solution. In the case of the 100 mL sample solution of wastewater, the cumulative percentage removal of Cr (VI) obtained in the first, second and third stage were 85.75%, 98.66% and 99.97% respectively. Likewise, the cumulative percentage of removal of total chromium in the first, second and third stage was 85.26%, 98.66% and 98.19%, as represented in Table 5. For, 1000 mL sample solution of wastewater, the cumulative percentage removal of Cr (VI) obtained in the first, second and third stage were 88.04%, 99.59% and 99.98% respectively. While the cumulative percentage of removal of total chromium in the first, second and third stage was 87.17%, 96.38% and 98.75%, as represented in Table 6. For the third supernatant, complete removal of total chromium is not observed as part of the hexavalent form of the chromium was converted to the trivalent form and desorbed into the solution. In comparison to the results obtained for 100 mL of sample solution of acidified potassium dichromate using identical operating condition, similar cumulative removal efficiencies were observed with 1000 mL of acidified Potassium dichromate solution. Figure 7 depicts the cumulative percentage removal of chromium with the number of stage. Almost identical cumulative removal efficiencies are obtained in the second and third stage for different volumes of synthetic wastewater solution as depicted in Figure 7. This points out towards the fact, that the procedure is scalable and can be scaled without any significant change in cumulative removal efficiency of Cr(VI) and total chromium from aqueous solution. The stage wise removal efficiencies for Cr(VI) is much higher that obtained for total chromium. A plausible explanation for this being, the reduction of Cr(VI) to Cr(III) on the surface of wool. For the 100 mL of wastewater solution, the stage wise percentage removal for Cr(VI) were 85.75%, 90.65% and 97.52% in the first, second and third stage respectively. The stage wise removal for total chromium were 85.26%, 72.91% and 54.45% in the first,
second and third stage respectively as represented in Table 5. For the 1000 mL of wastewater solution, the stage wise percentage removal for Cr(VI) removal were 88.04%, 88.26 % and 98.34% in the first, second and third stage respectively. The stage wise removal for total chromium were 87.17%, 71.82% and 66.78% in the first, second and third stage respectively as represented in Table 6. To ensure the industrial application of this method, pilot scale studies need to be conducted and analyzed accordingly.

![Figure 7: Percentage removal of chromium in different stages of SBC. Initial Cr(VI) = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0 and T = 25.0°C and shaking speed = 150 rpm. SBC 1 = 0 - 25 min, SBC 2 = 25 – 50 min and SBC 3 = 50 – 75 min. Volume = A: 100 mL, B: 1000 mL of wastewater sample solution.](image)

4.2 **Regeneration Studies**

4.2.1 **Effect of time.** The adsorbed wool was subjected to a desorption by the use of 100 mL of 0.1 M KCl solution, adsorbent dosage of 8 g/L, shaking speed of 150 rpm and temperature of 50 ± 2°C. Samples were collected for analysis at the end of 2, 5, 10, 15 and 25 minutes. Figure 8 depicts the effect of time on the concentration of Cr(VI) and total chromium in a desorption process. The concentration of Cr(VI) and total chromium increased with time. This happens because the KCl reacts with adsorbed Cr(VI) laden wool sample, thereby causing the release of Cr(VI) into the solution [73]. Table 7 provides the mass of Cr(VI) and total chromium in mg desorbed at different time interval. Table 8 provides the concentration of Cr(VI) and total chromium in ppm and the desorption efficiencies in percentages at different time intervals. Maximum
removal efficiency for Cr(VI) and total chromium is obtained towards the end of 25 minutes. Hence, the optimal contact time chosen for desorption was 25 minutes.

Table 7: Mass of chromium desorbed in mg at different time interval. Concentration of KCl solution = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, contact time = 25min. Adsorption temperature = 25°C, desorption temperature = 50°C, mass of Cr (VI) adsorbed on wool = 1.58 ± 0.14 mg, mass of total Cr adsorbed on wool = 1.67 ± 0.25 mg.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass of Cr(VI) Desorbed (mg)</th>
<th>Mass of Total Cr desorbed (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.6 ±0.22</td>
<td>2.79 ± 0.19</td>
</tr>
<tr>
<td>5</td>
<td>3.4 ± 0.01</td>
<td>3.82 ± 0.23</td>
</tr>
<tr>
<td>10</td>
<td>3.87 ± 0.17</td>
<td>4.29 ± 0.10</td>
</tr>
<tr>
<td>15</td>
<td>4.3 ± 0.16</td>
<td>4.32 ± 0.14</td>
</tr>
<tr>
<td>25</td>
<td>4.97 ± 0.12</td>
<td>4.41 ± 0.11</td>
</tr>
</tbody>
</table>

Table 8: Effect of contact time on chromium concentration. Concentration of KCl solution = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, pH = 2.0 and T = 50.0°C, shaking speed = 150 rpm and contact time = 25min.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration Cr(VI) (ppm)</th>
<th>Desorption Efficiency Cr(VI) (%)</th>
<th>Concentration Total Cr (ppm)</th>
<th>Desorption Efficiency Total Cr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26.10 ± 2.22</td>
<td>31.42 ± 2.06</td>
<td>27.87 ± 1.91</td>
<td>33.1072 ± 1.95</td>
</tr>
<tr>
<td>5</td>
<td>33.94 ± 0.33</td>
<td>40.93 ± 0.98</td>
<td>40.21 ± 2.45</td>
<td>45.36 ± 2.20</td>
</tr>
<tr>
<td>10</td>
<td>38.40 ± 1.56</td>
<td>46.27 ± 0.95</td>
<td>47.67 ± 1.09</td>
<td>50.97 ± 0.30</td>
</tr>
<tr>
<td>15</td>
<td>42.84 ± 1.63</td>
<td>51.62 ± 0.49</td>
<td>50.80 ± 1.67</td>
<td>51.31 ± 1.21</td>
</tr>
<tr>
<td>25</td>
<td>49.76 ± 1.08</td>
<td>60.02 ± 2.31</td>
<td>55.09 ± 1.37</td>
<td>52.36 ± 0.42</td>
</tr>
</tbody>
</table>
Figure 8: Effect of contact time on chromium concentration. Concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, pH = 2.0 and T = 50.0°C, shaking speed = 150 rpm and contact time = 25 minutes.

4.2.2 Effect of temperature. The desorption of chromium from keratinous adsorbents is a function of temperature [65]. Figure 9 depicts the effect of temperature on the desorption efficiency.

Figure 9: Effect of temperature on Desorption Efficiency (%). Concentration KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm and contact time = 25 min.
The increase in the temperature resulted in an increase in the desorption efficiency of chromium from wool. The effect of temperature on the desorption of chromium from wool was tested using 0.1M KCl, which was studied at temperatures 25°C, 35°C, and 50°C. The experimental condition used were 100 mL volume of KCl solution, adsorbent dosage of 8g/l, shaking speed of 150 rpm and contact time of 25 minutes.

Table 9 provides the mass of Cr(VI) and total chromium in mg desorbed at different temperatures. Table 10 provides the concentration of Cr(VI) and total chromium in ppm and the percentage desorption efficiencies at different temperature.

Table 9: Mass of chromium desorbed in mg at different temperature. Initial concentration of KCl = 0.1 M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, contact time = 25min. Adsorption temperature = 25°C, mass of wool = 0.8 g, mass of Cr (VI) adsorbed on wool = 1.2 ± 0.5 mg, mass of total Cr adsorbed on wool = 1.39 ± 0.2 mg.

<table>
<thead>
<tr>
<th>Desorption Temperature (°C)</th>
<th>Mass of Cr(VI) desorbed mg</th>
<th>Mass of Total Cr desorbed mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.08 ± 0.18</td>
<td>3.02 ± 0.32</td>
</tr>
<tr>
<td>35</td>
<td>2.47 ± 0.05</td>
<td>3.59 ± 0.09</td>
</tr>
<tr>
<td>50</td>
<td>4.10 ± 0.08</td>
<td>3.95 ± 0.09</td>
</tr>
</tbody>
</table>

Table 10: Effect of temperature on desorption efficiency (%). Initial concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/l, shaking speed = 150 rpm and contact time = 25min.

<table>
<thead>
<tr>
<th>Temp Concentration Cr(VI) ppm</th>
<th>Desorption Efficiency Cr(VI) %</th>
<th>Final Concentration Total Cr ppm</th>
<th>Desorption Efficiency Total Cr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>20.75 ± 3.18</td>
<td>22.47 ± 4.35</td>
<td>30.21 ± 1.77</td>
</tr>
<tr>
<td>35</td>
<td>24.68 ± 0.94</td>
<td>27.11 ± 0.96</td>
<td>35.94 ± 0.45</td>
</tr>
<tr>
<td>50</td>
<td>51.19 ± 1.08</td>
<td>49.12 ± 2.19</td>
<td>49.33 ± 0.97</td>
</tr>
</tbody>
</table>
The percentage desorption efficiency for Cr(VI) obtained were 22.47%, 24.68% and 51.19% at 25°C, 35°C, and 50°C respectively. Likewise, the desorption efficiency obtained for total chromium were 34.37%, 40.61% and 49.33% at 25°C, 35°C, and 50°C respectively. The maximum desorption efficiency is observed at 50°C. Hence it was chosen as optimal temperature to carry out the successive experiments of adsorption desorption cycle.

4.2.3 Effect of concentration. KCl was used to desorb chromium from wool. Desorption studies were carried out for 0.1M and 1M KCl solution, to understand the effect of concentration on desorption efficiency. The experimental condition used were 100 mL volume of KCl, adsorbent dosage of 8 g/L, shaking speed of 150 rpm and contact time of 25 minutes. Figure 10 depicts the effect of concentration of KCl on the desorption efficiency.

![Figure 10: Effect of concentration of KCl on desorption efficiency (%).](image)

<table>
<thead>
<tr>
<th>Concentration of Potassium chloride (M)</th>
<th>Desorption Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Total Cr: 40, Cr(VI): 45</td>
</tr>
<tr>
<td>1</td>
<td>Total Cr: 50, Cr(VI): 55</td>
</tr>
</tbody>
</table>

Table 11 provides the mass of Cr(VI) and total chromium in mg desorbed at different concentration of KCl. Table 12 provides the concentration in ppm and percentage desorption efficiency of Cr(VI) and total chromium at different concentration. The highest desorption efficiency for both Cr(VI) and total chromium is obtained using 1M KCl solution. However, the range of percentage desorption efficiency in case of 0.1 M KCl and 1M KCl is small. From a feasibility perspective, 0.1M KCl can be used for carrying out desorption on a pilot scale. The apparent
decrease in percent desorption efficiency of total chromium in case of 1M KCl was due to the conversion of Cr(VI) to Cr(III) as described by Lemusto et al. [74]. The chromium(III) reacts with KCl to produce chromium chloride which precipitates out of the solution as CrCl\textsubscript{3} and cannot be read on the ICP or the UV. Figure 11 shows the color of the adsorbent wool samples. A shows the color of the wool samples after adsorption. The wool is dark yellow in color, this is due to the uptake of Cr(VI) ions from the wastewater solution on to the surface of the wool. B shows the color of the wool samples after desorption, which is faint yellow, this indicates Cr(VI) has been released from the surface of wool into the solution.

Table 11: Mass of chromium desorbed in mg at different concentration. Volume of KCl = 100 mL, shaking speed = 150 rpm, contact time = 25min. Desorption temperature = 50.0°C, mass of wool = 0.8 g, mass of Cr (VI) adsorbed on wool = 1.24 ± 0.11 mg, mass of total Cr adsorbed on wool = 1.51 ± 0.11 mg.

<table>
<thead>
<tr>
<th>Concentration KCl</th>
<th>Mass of Cr(VI) desorbed</th>
<th>Mass of Total Cr desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>mg</td>
<td>Mg</td>
</tr>
<tr>
<td>0.1</td>
<td>3.95 ± 0.09</td>
<td>4.01 ± 0.08</td>
</tr>
<tr>
<td>1</td>
<td>4.79 ± 0.05</td>
<td>4.73 ± 0.07</td>
</tr>
</tbody>
</table>

Table 12: Effect of concentration of KCl on Desorption Efficiency (%). Concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, T= 50.0°C and contact time=25min.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Final Concentration Cr(VI) ppm</th>
<th>Desorption Efficiency Cr(VI) %</th>
<th>Final Concentration Total Cr ppm</th>
<th>Desorption Efficiency Total Cr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>49.33 ± 1.08</td>
<td>48.36 ± 2.19</td>
<td>51.19 ± 1.37</td>
<td>49.12 ± 0.30</td>
</tr>
<tr>
<td>1</td>
<td>46.34 ± 0.52</td>
<td>52.84 ± 0.78</td>
<td>47.81 ± 0.96</td>
<td>51.50 ± 0.69</td>
</tr>
</tbody>
</table>
4.3. Adsorption Desorption Cycle

4.3.1. Effect of contact time. The adsorbent wool was subjected to three simultaneous cycles of adsorption-desorption. The experimental condition used in case of the adsorption step were initial chromium concentration of 100 ppm of Potassium dichromate acidified at pH 2, adsorbent dosage of 8 g/L, temperature of 25 ± 2°C and shaking speed of 150 rpm. The experimental condition used in case of the desorption step were 100 mL of potassium chloride, adsorbent dosage of 8g/L, temperature of 50 ± 2°C and shaking speed of 150 rpm. Effect of time on the Cr(VI) concentration during the adsorption desorption cycle is depicted in Figure 12. Table 13 provides the mass of Cr(VI) and total Cr adsorbed and desorbed in mg into the solution towards the end of each adsorption-desorption cycle. Table 14 provides the concentration of Cr(VI) and total chromium in ppm at the end of each adsorption-desorption cycle. During adsorption, the concentration of hexavalent chromium gradually decreases with contact time for all three cycles. This is because Cr(VI) present in the wastewater get adsorbed on the wool samples and forms a complex with it. On the surface of the wool, part of the Cr(VI) gets reduced to Cr(III). Then the Cr(III) gets desorbed from the wool’s surface and moves into the solution. Due to the adsorption of Cr(VI) on the wool, the concentration of Cr(VI) decreases with time in the analyte samples[3]. During desorption, the concentration of hexavalent chromium gradually increases with contact time for all three cycles. KCl reacts with the wool-Cr(VI) complex that was formed
due to adsorption, causing the release of Cr(VI) species into the solution. Hence, the concentration of Cr(VI) increases with time [73].

Table 13: Mass of chromium adsorbed and desorbed during each adsorption-desorption cycle. Volume of sample = 100 mL, contact time = 25 min, desorption temperature = 50°C, mass of wool = 0.8 g, mass of Cr (VI) adsorbed on wool = 1.24 ± 0.11 mg, mass of total Cr adsorbed on wool = 1.51 ± 0.11 mg.

<table>
<thead>
<tr>
<th>Cycle No</th>
<th>Mass of Cr(VI) adsorbed</th>
<th>Mass of Cr(VI) desorbed</th>
<th>Mass of Total Cr adsorbed</th>
<th>Mass of Total Cr desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
</tr>
<tr>
<td>Cycle 1</td>
<td>1.67 ± 0.25</td>
<td>4.97 ± 0.12</td>
<td>1.58 ± 0.14</td>
<td>4.41 ± 0.11</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>2.07 ± 0.15</td>
<td>3.60 ± 0.31</td>
<td>1.70 ± 0.08</td>
<td>4.33 ± 0.12</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>1.80 ± 0.21</td>
<td>3.97 ± 0.09</td>
<td>1.91 ± 0.08</td>
<td>4.91 ± 0.13</td>
</tr>
</tbody>
</table>

Figure 12: Variation of concentration of Cr(VI) with time over three adsorption-desorption cycle.

Figure 12: Variation of concentration of Cr(VI) with time over three adsorption-desorption cycle.
Table 14: Concentration of Cr (VI) and total Cr at the end of each adsorption-desorption cycle.

<table>
<thead>
<tr>
<th>Cycle No</th>
<th>Final Concentration Cr(VI) ppm</th>
<th>Final Concentration Total Cr ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption Cycle 1</td>
<td>21.27 ± 3.00</td>
<td>19.80 ± 1.78</td>
</tr>
<tr>
<td>Desorption Cycle 1</td>
<td>49.76 ± 1.08</td>
<td>55.09 ± 1.37</td>
</tr>
<tr>
<td>Adsorption Cycle 2</td>
<td>21.34 ± 0.72</td>
<td>25.90 ± 1.83</td>
</tr>
<tr>
<td>Desorption Cycle 2</td>
<td>45.02 ± 3.90</td>
<td>54.30 ± 1.68</td>
</tr>
<tr>
<td>Adsorption Cycle 3</td>
<td>22.19 ± 2.60</td>
<td>23.90 ± 3.90</td>
</tr>
<tr>
<td>Desorption Cycle 3</td>
<td>49.90 ± 2.60</td>
<td>61.38 ± 1.63</td>
</tr>
</tbody>
</table>

4.3.2. Removal efficiency. Three cycles of simultaneous adsorption desorption cycle were carried using the same adsorbent. Table 15 represents the concentration and percentage removal efficiency of chromium during adsorption cycles at the end of each cycle.

Table 15: Final concentration and percentage removal efficiency of chromium during adsorption cycles. Initial chromium concentration = 100 ppm, pH = 2.0, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, T = 25.0°C, shaking speed = 150 rpm and contact time = 25 minutes.

<table>
<thead>
<tr>
<th>Adsorption Cycle No</th>
<th>Final Concentration Cr(VI) ppm</th>
<th>Adsorption Efficiency Cr(VI) %</th>
<th>Final Concentration Total Cr ppm</th>
<th>Adsorption Efficiency Total Cr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 1</td>
<td>21.27 ± 3.00</td>
<td>82.98 ± 2.40</td>
<td>19.80 ± 1.78</td>
<td>84.16 ± 1.42</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>21.34 ± 0.72</td>
<td>82.92 ± 0.60</td>
<td>25.90 ± 1.83</td>
<td>79.28 ± 1.46</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>22.19 ± 2.60</td>
<td>82.25 ± 2.05</td>
<td>23.90 ± 3.90</td>
<td>80.88 ± 0.82</td>
</tr>
</tbody>
</table>

The effect of removal efficiency versus the number of cycles is as plotted in Figure 13. The adsorbent nearly shows similar removal efficiency for both hexavalent chromium and total chromium towards the end of each adsorption-desorption cycle. Thus, the same adsorbent can be used up to three cycles of adsorption desorption.
Figure 13: Removal efficiency of chromium during adsorption cycles. Initial chromium concentration = 100 ppm, pH = 2.0, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, T = 25.0°C, shaking speed = 150 rpm and contact time = 25 minutes.
Chapter 5: Conclusions and Recommendations

Wool fibers were utilized as an adsorbent for the removal of hexavalent chromium. For measuring the concentration of hexavalent and total chromium, the analytical instruments used include the UV Visible-spectrophotometer and the ICP. SBC experiment was performed using a lab scale setup to ensure the complete removal of Cr(VI). A four conical flask system were utilized to resemble a four stage SBC. The experimental conditions include 100 mL of 100 ppm of acidified potassium dichromate solution at pH 2, temperature of $25 \pm 2^\circ C$, adsorbent dosage of 8 g/L, shaking speed of 150 rpm and contact time of 25 minutes maintained in each stage. On analysis of the results, it could be concluded that a three conical flask system is sufficient for the complete removal of hexavalent chromium. In comparison with the literature review of the previous study done in this area, the SBC is beneficial over a single contactor, as it eliminates the requirement of a long term mode of 5 days for complete reduction of Cr(VI) from wastewater. The SBC experiment was scaled up and performed for 1000 mL of synthetic wastewater solution, with similar experimental conditions. The results obtained from the scale up experiment were comparable to the results obtained from 100 mL of synthetic wastewater solution without any significant change in removal efficiency of Cr(VI) and total chromium. Therefore, the setup can be scaled for higher volume of synthetic wastewater solution utilizing the same experimental conditions. Regeneration studies on wool were carried out to observe the effect of time, temperature and concentration on the desorption efficiency. Contact time of 25 minutes, temperature of $50^\circ C$ and 1M concentration of KCl are optimal conditions to carry out desorption. Adsorption desorption cycle experiment were carried out to understand the effectiveness of wool. Wool retains its adsorption efficiency for three simultaneous adsorption desorption cycles.

Few recommendations for future work in this area is summarized as follows:

- SBC with similar experimental condition can be used for treating higher concentration of chromium containing influent wastewater.
- An industrial scale automated SBC can be designed, where a PID controller with valves can be used between each of the stages.
- A pilot scale column experiment with wool as a fixed bed of adsorbent can be utilized for treating industrial wastewater. The optimal parameters such as bed
height, flow rate and influent concentration required for the operation are obtained from the column experiment.

- Finally, the adsorption-desorption studies can be repeated for more number of cycles to utilize the full effective adsorption capacity of wool.
References


A.1 Calibration Curve for Hexavalent Chromium

The absorbance of the sample solution Cr(VI) ranging from 0.2 to 1 ppm were read at a wavelength of 540 nm. Table 16 provides the absorbance of Cr(VI) at different concentration. The Calibration curve for hexavalent chromium is obtained by plotting the absorbance versus the concentration of Cr(VI) in ppm. Figure 14 depicts the Calibration curve of Cr(VI). A linear relation between absorbance and concentration is followed and the value of $R^2 = 0.9887$ was attained. The extension index obtained is $0.756\left(\frac{l}{m_g \, cm}\right)$.

Table 16: Absorbance of Cr(VI) at different concentration.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicate 1</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1677</td>
</tr>
<tr>
<td>0.4</td>
<td>0.3171</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4837</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6245</td>
</tr>
<tr>
<td>1</td>
<td>0.7933</td>
</tr>
</tbody>
</table>

Figure 14: Calibration Curve for Cr(VI).
### Table 17: Absorbance of Cr(VI) and intensity of total concentration in SBC during each stage for 100 mL volume of synthetic wastewater solution. Initial chromium concentration = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0, T = 25.0°C and shaking speed = 150 rpm.

<table>
<thead>
<tr>
<th>No Of Stages</th>
<th>Cr(VI) Absorbance</th>
<th>Total Cr Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>1</td>
<td>0.0966</td>
<td>0.1232</td>
</tr>
<tr>
<td>2</td>
<td>0.0096</td>
<td>0.0144</td>
</tr>
<tr>
<td>3</td>
<td>0.0002</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

### Table 18: Absorbance of Cr(VI) and intensity of total chromium in SBC during each stage for 1000 mL volume of synthetic wastewater solution. Initial chromium concentration = 100 ppm, adsorbent dosage = 8.0 g/L, pH = 2.0, T = 25.0°C and shaking speed = 150 rpm.

<table>
<thead>
<tr>
<th>No Of Stages</th>
<th>Cr(VI) Absorbance</th>
<th>Total Cr Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>1</td>
<td>0.0876</td>
<td>0.0932</td>
</tr>
<tr>
<td>2</td>
<td>0.0087</td>
<td>0.0124</td>
</tr>
<tr>
<td>3</td>
<td>0.0001</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
A.3 Regeneration Studies

A.3.1 Effect of contact time

Table 19: Absorbance of Cr(VI) and intensity of total chromium in Effect of contact time on chromium concentration. Concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, pH = 2.0, T = 50.0°C, shaking speed = 150 rpm and contact time = 25 minutes.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Cr(VI)</th>
<th>Total Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>2</td>
<td>0.2210</td>
<td>0.1864</td>
</tr>
<tr>
<td>5</td>
<td>0.2565</td>
<td>0.2536</td>
</tr>
<tr>
<td>10</td>
<td>0.3067</td>
<td>0.2793</td>
</tr>
<tr>
<td>15</td>
<td>0.3380</td>
<td>0.3080</td>
</tr>
<tr>
<td>25</td>
<td>0.3827</td>
<td>0.3811</td>
</tr>
</tbody>
</table>

A.3.2 Effect of temperature

Table 20: Absorbance of Cr(VI) and intensity of total chromium in Effect of temperature on Desorption Efficiency (%). Concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm and contact time = 25 minutes.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Cr(VI)</th>
<th>Total Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>25</td>
<td>0.1435</td>
<td>0.1702</td>
</tr>
<tr>
<td>35</td>
<td>0.1900</td>
<td>0.1831</td>
</tr>
<tr>
<td>50</td>
<td>0.3811</td>
<td>0.3647</td>
</tr>
</tbody>
</table>
A.3.3 Effect of concentration

Table 21: Absorbance of Cr(VI) and intensity of total chromium in Effect of concentration of KCl on Desorption Efficiency (%). Concentration of KCl = 0.1M, volume of solution = 100 mL, adsorbent dosage = 8.0 g/L, shaking speed = 150 rpm, T= 50.0°C and contact time = 25min.

<table>
<thead>
<tr>
<th>Concentration KCl (M)</th>
<th>Cr (VI) Absorbance</th>
<th>Total Cr Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3647</td>
<td>0.3811</td>
</tr>
<tr>
<td>1</td>
<td>0.3526</td>
<td>0.3630</td>
</tr>
</tbody>
</table>
### A.4 Adsorption- Desorption Cycle

Table 22: Absorbance Cr(VI) and intensity of total Cr at the end of each adsorption-desorption cycle.

<table>
<thead>
<tr>
<th>Cycle No</th>
<th>Cr (VI)</th>
<th>Total Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Replicate 1</td>
<td>Replicate 2</td>
</tr>
<tr>
<td>Adsorption Cycle 1</td>
<td>0.1364</td>
<td>0.191</td>
</tr>
<tr>
<td>Desorption Cycle 1</td>
<td>0.3827</td>
<td>0.3811</td>
</tr>
<tr>
<td>Adsorption Cycle 2</td>
<td>0.161</td>
<td>0.1682</td>
</tr>
<tr>
<td>Desorption Cycle 2</td>
<td>0.3402</td>
<td>0.3107</td>
</tr>
<tr>
<td>Adsorption Cycle 3</td>
<td>0.141</td>
<td>0.1757</td>
</tr>
<tr>
<td>Desorption Cycle 3</td>
<td>0.3671</td>
<td>0.3731</td>
</tr>
</tbody>
</table>
Vita

Priyasha Ray completed her B.E. degree in Chemical Engineering with First Class with Distinction from University of Pune, India in 2013. Through her undergraduate studies, she was an organizing committee member of the extra-curricular clubs in her college.

In September 2014, she joined the Master of Science program in Chemical Engineering at the American University of Sharjah. During the span of her program she has worked as a Graduate Teaching Assistant and Graduate Research Assistant at Chemical Engineering and Civil Engineering department.

Ms. Ray’s areas of interest include air and wastewater pollution treatment, solid waste management, industrial hygiene and process safety.