JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

M.Sc. THESIS ON

APPLICATION OF LOCALLY AVAILABLE ADSORBENTS FOR ADSORPTIVE

REMOVAL OF Cr (VI) FROM WATER

By

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FEBRUARY, 2021

JIMMA, ETHIOPIA

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REMOVAL OF Cr (VI) FROM WATER

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THESIS SUBMITTED TO JIMMA UNIVERSITY COLLEGE OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

FEBRUARY, 2021
JIMMA, ETHIOPIA

Declaration

This thesis entitled: (Application of locally available adsorbents for adsorptive removal of Cr (VI) from water, submitted to College of natural science Department of Chemistry in   partial fulfillment of the requirements for the Degree of Master of science in chemistry (Analytical). I Abayneh Kebede here by declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the thesis have been duly acknowledged.

Submitted by:

Abayneh Kebede   Signature   Date

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Acknowledgement

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Abstract

The presence of chromium (VI) in water is extremely harmful because it can cause illnesses, disorder and diseases to human. In this study, the performance of low- cost natural sorbents was evaluated for the removal of Cr(VI) from aqueous solutions. Batch adsorption experiments were performed in order to examine the removal process under different parameters which are contact time, pH and initial concentration. The Cr(VI) ion uptake was pH dependent and reached maximum at pH 2 and 3 for both Tella residue and pea (Pisum. sativum) seed shell, respectively. The adsorbents were characterized using FTIR and XRD. In order to describe the relationship between the concentration of Cr(VI) ions in the solution and the amount of Cr(VI) ions adsorbed to both adsorbents, Langmuir and Freundlich isotherm models were used for the equilibrium tests. The results of the studies showed that with lower initial concentration, lower solution pH, and at optimum contact time, the removal efficiency of Cr(VI) was found to increase. The Freundlich isothermal equation model describes a stronger adsorption mechanism than the Langmuir isotherm regression coefficient. Pseudo-first-order and pseudo-second-order models were used to evaluate biosorption kinetics and it was found that the pseudo-second-order model mechanism is the best-described Cr(VI) biosorption for powdered Tella residue and Pea (Pisum sativum) seed shell. Therefore, the batch studies showed that Tella residue and Pea (Pisum sativum) are favorable adsorbent for removal of Cr(VI) from aqueous solution.

KEYWORDS*; Batch, adsorption, Chromium (VI), Tella residue, pea (Pisum sativum) seed shell*

List of Acronyms

ASTM   American society for testing and materials

DPC   Diphenyl carbazide

FTIR   Fourier Transform Infrared Spectrophotometer

MCL   Maximum contaminant limits

pHzpc   Point of zero charge

PFO   Pseudo first order

PSO   Pseudo second order

RPM   Rotation Per Minutes of agitation speed

USEPA   United states Environmental Protection Authority

UV-vis   Ultra violate visible spectrophotometer

WHO   World Health Organization

XRD   X-ray diffraction

1 Introduction

Water is one of the most essential components of the environment which circulates among atmosphere, lithosphere and hydrosphere and it is required to fulfill different types of needs in every phase of the lifecycle[1]. With rapid development of the industry such as metal plating facilities, mining operations, electricity generation facilities, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc. direct and indirect releases of heavy metals to the environment from wastewater have been substantially increased[2.] The pollution from industrial and urban waste, effluents and from agrochemicals in to some water bodies and rivers creates harmful effects on human and animal health and ecology[2].

Chromium is a lustrous metal that occurs naturally in rocks, soil, volcanic dust and gases, as well as in animals and plants[5]. Chromium is involved in the natural metabolism of human fats and proteins at low levels, so only small amounts are needed for normal human functions. In the environment, chromium occurs mainly in two valence states, trivalent chromium (Cr(III) and hexavalent chromium Cr(VI). Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). The respiratory tract is also the major target organ for chromium (III) toxicity, similar to chromium (VI). Chromium (III) is an essential element in humans. The body can detoxify some amount of chromium (VI) to chromium (III) [3]. The hexavalent form is a known toxin, mutagen and carcinogen. Cr(VI) is a strong oxidant in the form of chromates(CrO_4^{2-}) and di-chromates($Cr_2O_7^{2-}$), it penetrates biological membranes and reacts with cell contents, proteins or nucleic acids, while being reduced to Cr(III)[4]. All Cr(VI) compounds are strong oxidizing agents and are recognized by the World Health Organization (WHO) as "carcinogenic to humans (Group 1)", and Cr(VI) is recognized as a pulmonary carcinogen. the maximum permissible limit of Cr(VI) in potable water is 0.05 mg/L and set maximum contaminant limits (MCL) for surface water of 0.1 mg/L and according to US EPA] set a maximum limit of discharge 0.1 mg/L Cr(VI) to inland surface waters[5]. The maximum permissible level of chromium in drinking water is 0.05 mg/L according to Ethiopian standard guidelines[6].

Different conventional methods are used for removal of hexavalent chromium(Cr(VI), such as chemical precipitation[7], adsorption and filtration[8], ion exchange[9]; Electrocoagulation[10], membrane separation [11] and electrodialysis.[12] However, these methods have some drawback such

as low efficiency, high operating and maintenance cost, generate sludge causing disposal problems, or produce a secondary pollutant, which limits their applicability in the real situation.[13] In comparison adsorption method is simple to operate, solves the challenge of sludge disposal, high efficiency and an effective method for the removal of Cr(VI) and other heavy metals from aqueous solutions.

To date, different wastewater treatment technologies have been used to remove heavy metals from industrial wastewater. Wastewater treatment through adsorption is one treatment technique used.

Different adsorbent like modified and natural diatomite, alumina, chitosan, clay materials, orange peel banana peel etc. have been used to remove Cr(VI) from wastewater. But those bio adsorbent which have high removal capacity, low cost and easy accessibility are no question in being a choice for removal of Cr(VI)from aqueous solution. This research work is intended to use low cost adsorbent (Tella residue and pea (*P. sativum*) seed shell for removal of Cr(VI) because it is low cost adsorbent which can be easily prepared from materials that can be collected without charge.

1.1 Statement of problem

The presence of high levels of heavy metal in surface water, ground water, and soil has toxic effects on the receiving environment and human health and become a major concern from industries. Several industrial wastewater streams may contain heavy metals like, Zn, Mn, Hg, Fe, Cr and including the waste liquids generated by electroplating, metal finishing or the mineral processing industries[14]. Most of the chromium is discharged into aqueous systems as Cr(III) and Cr(VI). chromium affects the healthy development of plants and animals at different stages at different degrees depending on its oxidation state and concentration[15]. Its toxicity arises from highly oxidizing property of Cr(VI), high mobility and the formation of other radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell.

Cr(VI) is highly water-soluble, highly mobile in aqueous systems, and highly toxic as it causes severe physiological and neurological ill effects on human and animal health, such as anemia; diarrhea; nausea; epigastric pain; ulcers; vomiting; eye and skin irritation; damage to nerve tissues, kidney, and liver; pulmonary congestion; internal hemorrhaging; and circulatory shutdown[16]. chromium has potential health risks associated with metal uptake via food chain, dermal absorption or inhaling. High levels of exposure to heavy metals have been known to cause cancer, organ damage, joint diseases, and in extreme cases, death[17]. The presence of chromium at different concentration levels in water have direct or indirect impact, As a result, continuous investigation of different adsorbent is very important in order to solve problems of chromium contaminated water[15]. Therefore, there is a need for the development of simple and available local materials such as Tella residue and Pea(*Pisum sativum(P. sativum)*) seed shell which could be used to eliminate Cr(VI) from water bodies. Moreover, understanding these methods is very essential to reduce chromium concentrations in environment and avoid water pollution, this hence, the development of simple, rapid, and effect adsorbents. Thus, in this study the removal of Cr(VI) from aqueous solutions using pea (*P. sativum*) seed shell and Tella residue or waste has been investigated.

1,2 Objectives of the study

1.2.1 General objective

➤ To investigate the efficiency of low-cost adsorbents for removal of Cr(VI) from aqueous solution

1,2,2 Specific objectives

➤ To prepare and evaluate the adsorptive capacity bio-sorbent such as; Avocado (*Persea americana*) seed, Mango (*Mangifera indica L*) seed shell, Egg shell, *Ensete ventricosum* midrib of leaf, Barely (*Hordeum vulgare* L. (Poaceae) bran, Coffee (*Coffea arabica* L) residue, Tella residue, Ash, Charcoal, Pea (*Pisum sativum*) seed shell, and korch (*Erythrina abyssinica)*
  ➤ To select efficient adsorbents depending their capability to remove Cr(VI) from contaminated water.
  ➤ To characterize selected low-cost bio sorbents.
  ➤ To assess the effects of various parameters such as contact time, pH, and initial Cr(VI) concentration on the adsorption efficiency of selected low-cost adsorbent.
  ➤ To assess the kinetics of the adsorption of Cr(VI) onto the adsorbent.
  ➤ To describe the responsible adsorption isotherm models that represent the adsorption of Cr(VI) onto low-cost adsorbent.

1.3 Significance of the study

Due to environmental issues and health threats, the removal of Chromium(VI) from industrial waste water is important. This research will ensure the alternative method of removing Chromium(VI) and show that Tella residue and Pea (*Pisum sativum*) seed shell can be low-cost adsorbent based on economic reasons and their availability.

- ✓ Its use in the treatment of industrial waste water can be an alternative to reduce the environmental and simultaneous impacts of chromium(VI) waste water.
- ✓ Decrease the concentration of it in the system.
- ✓ The re-usability of these goods by product is an environmentally sustainable waste solution.
- ✓ To extract Cr(VI) from aqueous solution, generate environmentally competitive and low-cost adsorbent.

2 Literature review

2.1 Chemistry of Chromium

Chromium (Cr) is a silver color hard metal with atomic number 24, molecular weight 51.1 and density 7.19 g/cm^3. Chromium is the 7th most abundant element and 21st most abundant metal of the Earth's crust[18]. Chromium is such a major toxic heavy metal for both humans and the environment and often found in industrial wastewater, which is introduced into water streams from mining, tanning, electroplating, wood preservatives, paints, textile dyeing, and plants producing industrial inorganic chemicals and pigments[19]. Chromium occurs most frequently as both trivalent [Cr(III)] and hexavalent [Cr(VI)] states in aquatic environment. Trace amounts of Cr(III) is an essential micronutrient for sugar, protein and fat metabolism in mammals, while Cr(VI) is a primary contaminant, which is considered potential carcinogen that induces primary liver cancer[20].

Chromium compounds have different physicochemical properties and toxicity for example. Cr(III) is a trace nutrient for the proper functioning of living organisms. It is nearly insoluble in the form of Cr (OH)$_3$ precipitate at neutral pH generally insoluble in water. Cr(VI) compounds have extreme hazardous effects on biochemical systems and highly soluble in full pH range[21]. The Cr(VI) anion in the aqueous solution is not a simple monovalent anion, but it can be found in the different forms according to the pH and concentration of the medium. Cr(VI) exists in the form of $HCrO_4^-$ and CrO_4^{2-} in the solution at low concentrations and near neutral pH values. When the solution phase is acidic, $HCrO_4$ is the main species in the aqueous phase[22]. Acidic solutions of dichromate are strong oxidants. During oxidation Cr(VI) is reduced to Cr(III) through the formation of intermediates Cr(V), Cr(IV), and Cr(II); however, basic solutions of chromate are less oxidizing Polymerization beyond dichromate is apparently limited to formation of tri- ($Cr_3O_{10}^{2-}$) and tetra- ($Cr_4O_{13}^{2-}$) chromate.[23] Most of the Cr(III) compounds are sparingly soluble in water, whereas the majority of Cr(VI) compounds are highly soluble. some of Cr(VI) compounds which are soluble in water are shown **in table 1** below.

Table 1 Hexavalent chromium compounds [24].

Compound	Form	Solubility in water
Sodium Chromate (Na_2CrO_4)	Yellow Crystal	Soluble
Calcium Chromate ($CaCrO_4$)	Yellow Crystal	Slightly soluble
Sodium Dichromate ($Na_2Cr_2O_7$)	Orange red crystal	Soluble
Potassium Chromate (K_2CrO_4)	Yellow Crystal	Soluble
Chromium Trioxide (CrO_3)	Dark red/brown crystal	Soluble
Potassium Dichromate ($K_2Cr_2O_7$)	Orange red crystal	Soluble
Strontium Chromate ($SrCrO_4$)	Yellow Crystal	Slightly soluble

2.2 Natural sources and industrial emissions of chromium

Chromium is a naturally occurring element in rocks, animals, plants, soil, and volcanic dust and gases. Weathering of rocks and soil erosion and leaching by rainwater are major natural processes favoring the input of chromium to rivers, lakes, streams, and ocean[25]. Most of the hazards coming to human and ecosystem are mostly due to ground water pollution. The untreated sewage, industrial effluents and agriculture wastes are often discharged into the water bodies. This contaminated water spread wide range of water borne diseases. Chromium is among the most toxic trace elements released to surface waters and ground waters due to its widespread use in industrial applications. Discharges of industries like mining stainless steel welding, electroplating, leather tanning, paper industry , and ferro-chrome and chrome pigment production contribute to chromium concentrations in water bodies (environment of aquatic) above the regional guideline values[26]. Hexavalent chromium plays a key role in metal finishing industry by modifying the surface of a product to enhance its appearance and reflectivity, such as color or brightness, corrosion resistance and good hardenability.

2.3 Advantages of chromium compounds

Chromium has become a major industrial metal due to its human use in the manufacture of ferrous metals and non-ferrous alloys and in the chemical industry. Chromium compounds are used in many

industry and manufacturing applications. including fabrications of steel alloy, where they improve corrosion and heat resistance. and in plated product fabrication where they are used for metal decoration or increased wear resistance are also used in nonferrous alloy metal fabrication to impart special qualities to the alloys; in production and processing of insoluble salts, as chemical intermediates; in the textile industry for dyeing, silk treating, in the leather industry for tanning to obtain leather of desirable quality; in the manufacture of green varnishes inks, paints and glazes; as catalyst for halogenations, alkylation and catalytic cracking of hydrocarbons; as fuel and propellant additives; and in ceramics[27].

Table 2 the use and color of different forms of chromium

Form	Appearance (color)	uses
Cr (III)	Green	Alloy manufacturing, brick lining, chrome plating, tanning, and textiles, copying machine toner
Cr (VI)	Red, orange or yellow	Chrome plating, Leather tanning, textiles and machine toner
Cr (0)	Metallic grey / silvery	Stainless steel production, Alloy production, etc

2.4 Chromium Toxicity and its Accumulation

The measurement of the total chromium cannot be used to determine the actual environmental impact. This is because the Cr(III) in its biologically active form will facilitates interaction of insulin with its receptor site, influencing glucose, protein and lipid metabolism, so Cr(III) is essential for animals and human beings. However, for the Cr(VI) is highly toxic and carcinogenic in which it will causes the gene mutation. Thus, chemical speciation of chromium in environmental samples is necessary to accurately assess for its pollution levels toward environment and human. Recently, there are sensitive- analytical methods for the determination and speciation of chemical forms of toxicity of this hexavalent chromium metal ions in environmental samples. Trivalent chromium has lower human toxicity due to its low solubility and less absorbed by organic molecules[16].

Ingestion of high amounts of Cr(VI) causes gastrointestinal effects in humans and animals, including abdominal pain, vomiting, and hemorrhage. Acute animal tests have shown Cr(VI) to have extreme toxicity from inhalation and oral exposure[28]. Also, it can cause respiratory problems, including irritation of the lining of the nose, runny nose, and breathing problems such as asthma, cough, shortness of breath and wheezing. Chromium can lead to cancer in lung, stomach and intestinal tract. Regarding Chromium threshold for drinking water, although most EU countries apply a legal limit of 50 µg/L of chromium, limits are going to be reduced soon to 25 µg/L, according to a recent recast of the Directive 2001/83/EC, which occurred in 2018. A few years ago, in some Italian cities, chromium levels were already at the limits of the Directive 2001/83/EC on the quality of water intended for human consumption[29].

2.5 Effects of Short-term Exposure

Soluble trivalent chromium substances cause eye and skin irritation, but this effect is generally associated with their acidic nature. Chromium compounds may cause skin rashes in some people who are 'chromium-sensitive'. on the other hand, hexavalent chromium is hazardous by all exposure routes:

> ➢ Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma).
> ➢ Ingestion may affect kidney and liver functions.
> ➢ Skin contact may result in systemic poisoning, damage or even severe burns.

2.6 Effects of long- term exposure

Exposure to hexavalent chromium, if prolonged or repeated, may lead to perforation of the nasal septum. The oral exposure of Cr(VI) can cause vomiting, oral ulcers, abdominal pain, indigestion, and diarrhea. Hematological effects such as leucicytosis and immature neutrophilswere also noted. Both soluble and insoluble Cr(VI) compounds are able to cause structural damage to DNA, leading to genotoxicity. Studies indicate that Cr(VI) induced DNA damage may result in clastogenesis, altered gene expression, and the inhibition of DNA replication and transcription.

Cr(VI) exists as highly soluble dichromate or chromate anions and is known to be toxic to all living organisms. It is proved to have a well-established carcinogen effect on human beings by the inhalation and oral route of exposure. The main concern about Cr(VI) compounds is associated with their mobility, which can easily lead to the contamination of both surface and ground waters[21]. Cr(VI) can be harmful to the biological system, and because of its oxidizing ability and simple penetration of biological membranes, water-soluble Cr(VI) is highly irritating and toxic to human body tissue. It leads to liver damage, pulmonary congestion, edema, and skin irritation resulting in ulcer formation. Cr(VI) is toxic to various plants, animals, bacteria, and poses a great threat to human health and the environment as a reported human carcinogen. Trivalent chromium, on the other hand, is primarily present as hydroxides and oxides that are relatively insoluble, immobile and non-toxic. The toxicity of trivalent chromium to a living cell is 500-1000 times less than that of hexavalent chromium. Hexavalent chromium has been recognized by heavy metals as more toxic, and thus receives much more attention.

2.7 Chromium impacts on the environment

Due to its high solubility, mobility and responsiveness, Cr(VI) negatively affects the environment. Human health and the atmosphere. The accumulation of alloys in economically essential crops and vegetables watered with tannery effluent has been analyzed. While Cr(III) is an essential human nutrient, there is no question that both acute and inveterate poisonous compounds are Cr(VI) compounds. The dose threshold outcome for this portion has not yet been adequately tested to enable regulations to be specified, but a few risk assessment analyses are currently being attempted. In recent days, the direct discharge of wastewater from tanneries to water bodies has become an emerging environmental issue. Most of these effluents are highly complex mixtures containing inorganic and organic compounds that theoretically make a pollution-intensive sphere for the tanning industry[30].

2.8 Chromium removal technologies

Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Consequently, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater. The most important of these technologies include; chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electrocoagulation. However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some drawbacks such as incomplete metal removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method[31].

2.8.1 Chemical precipitation

Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent Chemical precipitation is regarded as one of the established technologies for heavy metals and other pollutants removal from wastewater due to its simplicity and low cost. In this method, pollutants settle down as precipitates which then separated from the solution employing filtration, centrifugation, or other suitable methods. Coagulant as a precipitating agent causes the smaller particles suspended in solution to increase their particle size for settling down as sludge. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out. In the conventional water treatment process coagulation using alum and ferric (Fe(III)) coagulants has been used for Cr(III) removal, in which the removal is due to precipitation as $Cr(OH)_3$ and co-precipitation with $Al(OH)_3$ or $Fe(OH)_3$.

Usually, hydroxide precipitant is commonly used for its low cost, simplicity, and ease of pH control. The conventional chemical precipitation techniques include sulphide precipitant and hydroxide precipitant. In hydroxide precipitation process, addition of coagulants such as iron salts, alum, and organic polymers can increase the removal quantity of heavy metals from wastewater. Chemical precipitation of chromium by calcium hydroxide $[Ca(OH)_2]$, sodium

hydroxide (NaOH), magnesium oxide (MgO), or calcium magnesium carbonate [CaMg(CO$_3$)$_2$] is frequently practiced in many tanneries. The disadvantage of this processes are requirement of working with corrosive chemicals which increase operator safety concerns and an addition of treatment chemicals, especially lime, may increase the volume of waste sludge by up to 50 percent[32].

2.8.2 Membrane filtration

The word membrane originated from the Latin word membrane which means a skin. It selectively passes the materials. Membrane is used to separate single-celled organisms like bacteria to atom. Membra-one can be defined as a discontinuous phase between two adjacent phases that permits the exchange of matter, energy, and information. between the phases with selective or non-selective properties. the main membrane separation processes used for wastewater treatment are Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and electrodialysis(ED)[33].

2.8.2.1 Electrodialysis (ED)

Electrodialysis is an electrochemical process of membrane technology that removes ionic contaminants from an aqueous solution. ED has advanced rapidly due to the advent of upgraded ion exchange membrane properties, improved materials of construction, and advances in technology. In this process, ions are separated through an ion exchange membrane with the help of applied electrical potential between the anode and cathode. Electrodialysis is a membrane separation process in which ions are transported through ion selective membranes from one solution to another under the influence of an electric field. This transport generates two new solutions: one that is more diluted and one that is more concentrated than the original The disadvantage is the formation of metal hydroxides, which clog the membrane[34].

2.8.2.2 Ultrafiltration

Ultrafiltration is usually associated with the separation and concentration of macromolecules, using membranes with micro pores of the order of 1–100 nm. The transport mechanisms that are generally employed in these kinds of membranes are molecular exclusion and diffusion.

2.8.2.3 Reverse osmosis

Reverse osmosis is used to separate salts and small organic molecules from liquid streams, using membranes with dense active layers, where the preferred transport mechanisms are often attributed to solution/diffusion. Due to the high density of the active layer, operating pressures have to be much higher than those used in microfiltration and ultrafiltration. The nanofiltration process is an intermediate separation process between reverse osmosis and ultrafiltration, commonly used in the separation of organic solutes with low molecular weight (200–1000 Da) and in the partial demineralization (essentially polyvalent salts) of liquid streams.

2.8.3 Ion exchange

Ion exchange is a reversible chemical reaction through which ions in solution are exchanged for similar ions attached to a solid matrix. It is very effective for reducing heavy metals from wastewater as it is a cost-effective and convenient process in operations. The solid matrix particles commonly used are synthetic organic ion exchange resins. The exchange resins can take up positively or negatively charged ions from an electrolyte solution and discharge other ions with the same charges in an equivalent amount into the solution. Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide and dissolved organic carbon (DOC)[9].

Ion exchange is one of the "best available technologies" for the removal of chromium. It is a proven technology for small systems for the removal of low concentrations of chromium. Cation exchangers are effective for Cr(III), while anion exchangers are appropriate for Cr(VI) removal. For removal of Cr(VI), strong-basic anion exchangers, with an exchangeable counter ion of Cl⁻, are commonly used disadvantage of this process includes high cost and selectivity of ions[35].

2.8.4 Electrochemical method

Electrochemical methods involve the redox reactions for metal removal under the influence of external direct current in the electrolyte solution. The coagulation process destabilizes colloidal particles by adding a coagulant and results in the sedimentation process. For increase in the rate of coagulation, the flocculation process takes place which enhances the change of unstable particles into bulky floccules[31].

2.8.5 Flotation

Flotation has been widely applied for the removal of toxic metal ions from wastewater. The techniques of flotation are ion flotation, dissolved air flotation (DAF) and precipitate flotation. DAF is a more commonly used process than any other flotation techniques in the removal of heavy metals from aqueous solutions.

2.8.6 Adsorption

Adsorption is the process of transferring the ions from solution phase to solid phase. In this process a film called adsorbent surface is created. The formation of bonds between dissolved organisms or tiny particles and the surface of a solid is adsorption[36]. The adsorption method is used in a number of major industrial applications and is now increasingly used as an inexpensive and effective separation technique for the removal of metal ions from waste water on a wide scale.
Several treatment technologies have been developed to extract chromium and other heavy metals efficiently from solutions using commercially viable natural adsorbents such as agricultural waste such as sunflower stalks, eucalyptus bark, maize bran, coconut shell, rice straw, tree

leaves, saw dust, sand, clay mineral, charcoal, and various agricultural products such as peanut shell, wheat husk, sugarcane bagasse, biosorption, magnetic beads, carbon nanotubes, Sinorhizobium et*c*. Many scientists have studied and practiced these techniques for their chromium removal efficiencies in various parts of the world [37]. In addition to that there are different reports on the use of Wheat brane[38], rice straw, coffee husk[39] were also reported. In general, a wide range of adsorption techniques for extracting Cr(VI) from water and waste have been reported in the literature, including chemical precipitation, ion exchange, membrane separation, elctrocoagulation, reverse osmosis, electrodialysis[7, 9-12]. Therefore, in order to save money and/or recycle waste content, alternative adsorbents have been suggested for removal of Cr(VI) due to their limitations of these techniques. Various biomass adsorbents prepared from avocado kernel seeds (AKS), Juniperus procera sawdust (JPS) and papaya peels (PP) have been reported, showing that their capabilities have been found to be effective adsorbents for the removal of Cr(VI), their capacities were found to be 16.03, 10.08 and 7.16 (mg/g) respectively[40].

Several literature surveys use various biomass in aqueous solutions as well as in wastewater samples to extract Cr(VI) with their good adsorption ability, such as neem leaves powder with 0.85 mg/g [41]. For chromium removal, the use of waste material such as Macadamia nutshell biosorbents as an adsorbent was used, which was recorded to decrease slightly with a high capacity of 45.23 mg/g at pH 2 with an increased pH[42], Pine needle powder with capacity of 40 mg/g at pH 3[43], and Olive bagasse with capacity of 48.2 mg/g at pH 2 [44]. This shows that the adsorbent's Cr(VI) adsorption potential depends on pH. Adsorption isotherms of chromium ions on sawdust in aqueous solution indicate a smaller capacity of adsorption, around 0.229 mg/g at pH 2[45], and Potato peel powder with capacity of 3.28 mg/g at pH 2.5[46], Carbon anode dust and Waste mould sand with capacity of 4.29 and 1.19 mg/g respectively.[47] In the Jimma field, the use of fired clay soils to extract Cr(VI) from aqueous solution was investigated. The adsorption potential ranging from 0.67 to 0.83 mg/g were achieved for a 1 percent increase in clay content and the maximums measured by Langmuir ranged from 4.74, 4.81 and 8.77 mg/g, respectively[48].

2.8.7 Mechanism of Adsorption

Adsorption is one of the unit operation in waste water treatment which occupies an important position due to its cost, economic feasibility and its efficiency process for treatment of wastewater containing dissolved organic pollutants [49]. In the adsorption process, molecules are extracted from one phase (liquid phase) and concentrated at the surface of a second phase (solid phase, adsorbent) which occurs due to an attractive force existing between the adsorbent surface and the adsorbate molecules. Therefore, it is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction. The adsorption process consists of three consecutive step[50].

• Substances adsorb to the exterior of the adsorbent

• Substances move into the adsorbent pores

• Substances adsorb to the interior walls of the adsorbent

2.8.8 Types of Adsorption

➢ **Physisorption**

Physisorption or physical adsorption occurs when, as a result of energy difference and / or electrical attractive forces (weak Van der Waals forces), adsorbate molecules become physically fastened to the adsorbent surface. Physisorption takes place with the formation of single or multiple layers of adsorbate on the adsorbent surface and is characterized by a low activation energy (enthalpy) of adsorption[51].

➢ **Chemisorption**

Chemisorption or chemical adsorption occurs when a chemical reaction occurs between the adsorbed molecules and the adsorbent. Chemisorption takes place with the formation of a single layer of adsorbate attached to the adsorbent surface by chemical bonds. This type of interaction is strong with a covalent bond between adsorbate and the surface of the adsorbent is characterized by a high enthalpy of adsorption[52].

2.8.9 Factors affecting adsorption

Many physicochemical factors influence the amount of adsorption of a adsorbate (chromium) onto an adsorbent and these include: surface area of adsorbent, initial concentration, temperature, pH and contact time between adsorbate and adsorbent etc. Apart from the Physicochemical factors such as pH, the presence of other anions and cations, metal speciation, pollutant solubility and form, etc. may also have an influence. With living cell systems, the provision of nutrients and optimal growth conditions is an obvious requirement[53].

I.   Effect of pH

The pH factor is very important in the adsorption process of metal ions. Because the pH of metal ion solution affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during adsorption process.

pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized molecules. As a result, the rate of adsorption will vary with the pH of an aqueous solution. At low pH solution, the percentage of adsorbate removal will decrease for cationic species adsorption, while for anionic species percentage removal will increase. In contrast, at a high solution pH, the percentage removal will increase for cationic adsorption and decrease for anionic species[54]. Adsorption of chromium is highly influenced by the pH of the solution according to others studies on chromium removal efficiency which decreased with an increase in pH for hexavalent chromium[55] . In the case of chromate, the lower pH resulted in higher adsorption as the positively charged surface of the adsorbent

II. Effect of contact time

Adsorption is also affected by contact time between surface of adsorbent and the solution containing metals(adsorbate). In earlier works reported that adsorption proceeds fast and most metals are adsorbed at the very beginning of the process[56]. In adsorption systems, contact time plays a vital role irrespective of other experimental parameters affecting the adsorption kinetics.

The determination of the optimum contact time needed to achieve the highest removal of metal ions is very important in batch adsorption experiments.

III . Initial concentration

The initial concentration is important in adsorption, since a given mass of sorbent material can only adsorb a fixed amount of adsorbate. Normally, the adsorbate removal will decrease with increase in initial concentration. This is because for a given mass of adsorbent material; the amount of adsorbate (Cr(VI)) that can be adsorbed is fixed. The higher the concentration of the adsorbate, the smaller the volume it can remove. Other researchers indicate at a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial Cr(VI) concentration increases, the active sites of the adsorbent surface should be occupied for adsorption molecules will be lacking. But the actual amount of chromium adsorbed per unit mass of adsorbent increased with increase in concentration. This may be due to the high driving force for mass transfer at a high initial hexavalent chromium concentration [43].

IV. Particle size of adsorbents

The Particle size of adsorbent is very important in adsorption process. The particle size of a material influences many of its properties and can indicate the quality of the material and its performance. Whether for stability in suspension, reactivity, appearance, viscosity, flow, packing density, texture and flavor or many other characteristics, a very important component in understanding how your product performs. and also determine the adsorption capacity and even the rate of adsorption[57].

V. Shaking speed and Temperature

The amount of metal ions adsorbed increased with the increase in the agitation speed. Increase in the speed of agitation enhances the rate of adsorption. By increasing the speed of agitation, the randomness increases during the adsorption process, resulting in better contact between the adsorbate and adsorbent in the system and hence enhancing the rate of adsorption[58].

Increasing the temperature leads to a decrease in adsorption due to the adsorbed molecules having greater energies and therefore becoming more likely to release from the surface of the adsorbent.   Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent[59].

2.8.10 Advantages and disadvantages of adsorption

➢ Metals at low concentration can be selectively removed.
➢ Effluent discharge concentration meets the govt. regulation.
➢ System operates over the broad pH ranges (2-9).
➢ System is effective over a temperature ranges of 4-90 ℃.
➢ System offers low capital investment and low operation cost.

➢ Convert metal pollutant to metal product.
➢ System offers simple design, easy operation
➢ Requires regeneration

2.8.11 Activated carbon

Activated carbon is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. Activated carbons are more effective in the removal of heavy metals due to some specific characteristics that enhance the use of activated carbon for the removal of contaminants including heavy metals from water supplies and wastewater [65].

3. Materials and methods

3.1. Chemicals and instruments

3.1.1 Chemicals

The chemicals used for study were: potassium dichromate, $K_2Cr_2O_7$ (99.5%, FINKEM, England),), acetone from (LOB CHEM India) 1,5 diphenylcarbazide (DPC), (98%, Analar, England), sulphuric acid, H_2SO_4 (98%, UNI CHEM, Germany), HNO_3 69% LOBA, chem. India Hydrochloric acid, HCl (37%, Riedel-deHaën, Germany), Sodium hydroxide, NaOH (90%, BDH, England). All chemicals were used in this study.

3.1.2. Instruments

Double beam UV-Vis spectrophotometer (Model SPECORD 200/PLUS, analytiKjena, Germany) was used to evaluate the final Cr(VI) ions concentration, pH meter (Bante instruments, pH 902P, USA) used to adjust the solution in acidic /basic media, thermostatic water bath (Model GrantGLS400, England) used to carry out the adsorption at preset temperature, oven (model GENLAB WLDNES, England) was used for drying purpose. FTIR spectrophotometer (model: Perkin Elmer Spectrum two) used to identify functional groups and XRD-7000 used to determine the structure of crystalline and amorphous of the sample.

3.2 Adsorbent preparation

Locally available adsorbents such as Avocado (*Persea americana*) seed, Mango (*Mangifera indica L*) seed shell, Egg shell, *Ensete ventricosum* midrib of leaf, Barely (*Hordeum vulgare* L. (Poaceae) bran, drinking Coffee (*Coffea arabica* L) residue, Tella residue, wood Ash, Charcoal, Pea (*Pisum sativum*) seed shell, and korch (*Erythrina abyssinica)* were collected from different places of Jimma city. These all adsorbents were washed with tap water repeatedly and rinsed with distilled water to remove all impurities and coloring components and then dried in the shad for the required time. After drying, all the adsorbents were ground, sieved to the mesh size of ≤ 300 μm and stored in air tight container for screening of Cr(VI) adsorption study.

Tella residue were collected from Jimma city, (kochi area) which was washed and dried under shade. The dried Tella waste were ground to fine powder. The powders were sieved to get particles of homogeneous size. then stored in an airtight container prior to use.[66] Whereas, the Pea (*Pisum sativum*) seed hull was collected from Jimma town (Ajip area), small milling machine (Jimma city). The pea (*P. sativum*) seed hull washed with tape water and distilled water, repeatedly then dried. The dried pea (*P. sativum*) shell was ground to fine powder, then sieved (mesh size of ≤ 300 μm) to get homogenous size particles, then stored in air tight container for further use.

3.3. Adsorbent characterization
3.3.1. Physicochemical characteristics

For both samples, Tella residue and pea (*P. sativum*) seed shell adsorbent, the physicochemical characteristics such as moisture, ash, volatile matter, and fixed carbon contents were determined.

3.3.1.1. Moisture content

Moisture content was determined using ASTM D2867-91 method[67].
The moisture content was determined by loss on drying method. 5 g of Tella residue and pea

(*Pisum sativum*) seed shell were accurately weighed and placed into a clean evaporating dish of a known weight. Then the dish containing a known weight of the sample was maintained at temperature of 105 °C in an oven for one an hour. After which the sample was cooled at room temperature in desiccator and its weight was recorded. Then subsequent incubations were made at the interval of 30 minutes until constant weight was achieved. The moisture content was calculated using the equation (1)

$$\text{moisture content}(\%) = \frac{(w2 - w1) - (w3 - w1)(g)}{(w2 - w1)(g)} * 100 \tag{1}$$

Where w_1 = weight of crucible, w_2 = weight of crucible and sample before drying W_3 = weight of sample and crucible after drying

$$D\text{ry mater}(\%) = \frac{\text{oven dry weight}(g)}{\text{initial sample weight}(g)} * 100 \tag{2}$$

3.3.1.2. Ash content

Ash content determination was done according to the ASTM D2866-94 standard procedure.[68] A 5 g sample of Tella residue powder and pea (*P. sativum*) seed shell from the oven dried sample were placed in a crucible and transferred into muffle furnace at a temperature of 550 °C for two hours until white ash was obtained. Then the crucible was cooled at room temperature in desiccator and its weight was recorded. The %ash content (dry basis) was calculated as:

$$\text{Ash content}(\%) = \frac{(W3 - W1)(g)}{(W2 - W1)(g)} \times 100 \tag{3}$$

Where, W1 = weight of the crucible, W2 = weight of the crucible and sample before igniting, W3 = weight of crucible and sample after igniting

3.3.1.3 Volatile Matter content

5 g of oven-dried, powdered sample was taken in crucible. Then the crucible was kept in furnace for 10 min at the temperature of 550 °C. The crucible was taken out of the furnace and allowed to cool in a dissector[69].

The %volatile matter content in the sample was calculated by using the formula given below

$$\text{Volatile matter}(\%) = \frac{(W2 - W1) - (W3 - W1)}{W2 - W1} \times 100 \tag{4}$$

Where, w_1 represents weight of crucible, w_2 weight of sample and crucible, w_3 represents weight of crucible and sample after incineration for the given time.

3.3.1.4 Fixed carbon content

The fixed carbon of samples was calculated by subtracting the sum of moisture content, ash content (%) and volatile matter (%) from 100 [69].

$$Fixed\ carbon\ content = 100 - (\%moisture + \%Ash + \%volatile) \qquad (5)$$

3.3.1.5 pH of adsorbent

0.4 g of both Tella residue and pea (*P. sativum*) seed shell were transferred into 50 mL plastic bottles and then 40 mL of distilled water was added and shaken for 24 h in thermostatic water bath. the mixture was allowed to stabilize and then the pH was measured [70].

3.3.1.6. Point of zero charge (PHPZC) determination

The point of zero charge of the Tella residue and pea (*P. sativum*) seed shell adsorbent were determined by the solid addition method. A 40 mL of 0.1 M and 0.01 M NaCl solution transferred into plastic bottles which contain 0.1 g of each both samples. The initial pH (pH_0) values of the solution were adjusted from 3 to 12 by adding either 0.1 M HCl or NaOH. Then 0.1 g of Tella waste and pea (*P. sativum*) seed shell was added to each plastic bottles which was securely capped immediately. The plastic bottles were then placed into a constant temperature water bath shaker and shaken for 48 h. The pH values of the supernatant liquid were noted after 48 h the difference between the initial and final pH values in y-axis was plotted against the initial pHi (x-axis).

3.3.1.7. Determination of surface area

Specific surface area of adsorbent was calculated using the formula Sears method [70].

1.0 g of adsorbent was mixed with 100 mL of distilled water and 20 g NaCl. The mixture was shaken for five minutes. Its final pH was adjusted to 4 with 0.1 M HCl. It was then titrated against 0.1 M NaOH to raise the pH from 4 to 9 and the volume (mL) of 0.1 M NaOH used was measured in replicate and the average value was taken for the surface area calculation by sears method.

$$S = 32 \times v - 25 \tag{6}$$

Where, S is surface area of bio adsorbent per gram (m^2/g), V is volume (mL) of 0.1M NaOH required to raise the pH of the sample from 4 to 9. The numbers 32 and 25 are physical constants.

3.3.1.8. FT-IR Spectral Analysis

FT-IR characterization was performed in order to identify the functional groups existing on the bio adsorbent that might be involved in the chromium uptake process. The Adsorbents were characterized using (FT-IR) before and after adsorption process in average wave length from 4000 to 400 cm^{-1} to observe the changes in functional groups. The prepared both Tella residue and pea (*P. sativum*) seed. samples powder was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then press to a small thickness to make the sample a pellet that required for FT-IR study. Then the adsorbent was scanned in the spectrum range of 4000-400 cm^{-1}. This spectrum is a graph which comprises percentage of transmittance along Y- axis and wavelength along X- axis.

3.3.1.9. X- ray diffraction (XRD) analysis

XRD spectra of powdered Tella residue and pea (*P. sativum*) seed shell was characterized by using X-Ray Diffractometer at Jimma university Techno campus, material science department. The powder samples were packed and loaded into the diffractometer. The powder was packed into the holder then pressed down and flattened in order to present a smooth diffraction surface. Then, the diffractometer was run over a 2θ range of 10° to 90°.

3.4. Analytical procedures

3.4.1. Preparation of Stock solution

A stock solution of Cr(VI) with a concentration of 1000 mg/L was prepared by dissolving 2.83 g of potassium dichromate ($K_2Cr_2O_7$, 99.5%) in 1000 mL distilled water. Then standard solution containing 100 mg/L of Cr(VI) was prepared in 500 mL volumetric flask by dissolving 50 mL of stock solution with distilled water and filled up to the mark. The working solution was prepared by diluting 50 mL from 100 mg/L standard solution with distilled water in 1000 mL volumetric flask to give the appropriate working solution containing 5 mg/L of Cr(VI). The pH of the test solution was adjusted by 0.1 M HCl or NaOH and measured using a pH meter. During residual Cr(VI) determination, the color chelating agent was prepared by dissolving 0.25 g 1,5-diphenylcarbazide with 50 mL of acetone in volumetric flask, then stored in brown bottle in refrigerator according to literature[71].

3.5. Batch Adsorption Study

Depending on the parameters under study the effect of contact time, pH, and initial Cr(VI) ions concentration were varied to study the adsorption efficiency of the adsorbent. The batch adsorption studies were carried out using 40 mL of 5 mg/L Cr(VI) solution in plastic bottles under different period of time, a desired pH and initial Cr(VI) ions concentration values in thermo stated water bath shaker at 25 °C. The pH of the solution was adjusted using 0.1 M HCl or NaOH. The bottles were agitated at a speed of 200 rpm in thermostatic water bath shaker for 24 hours. When adsorption time was completed the aqueous phase was filtered through Whatman filter paper, No 1 and the residual Cr(VI) ions left in the filtrate was introduced to double beam UV-Visible spectrometer for determination of adsorption efficiency. The Cr(VI) removal efficiency (% removal), amount of Cr(VI) adsorbed per mass unit of adsorbent at time t (min) , q_t (mg/g) and at equilibrium q_e were determined using the following equation.

$$Cr(VI) \text{ removal } (\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (7)$$

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{8}$$

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{9}$$

Where, C_0, C_t, and C_e are the initial Cr(VI) concentration in solution before mixing with adsorbent (mg/L), the concentration of Cr(VI) at time t (min), and the concentration of Cr(VI) at equilibrium (mg/L), respectively; V is the volume of solution (L) and m (g) is the mass of adsorbent dosage[72].

3.5.1. Effect of contact time

The adsorption of Cr(VI) ions by the adsorbents were studied at range of adsorption periods 1 – 720 min for both Tella residue and pea *(P. sativum)* seed shell. This was done by weighing 0.1 g of each of the adsorbents in plastic bottles containing 40 mL of 5 mg/L of Cr(VI) ion solutions at optimized pH 2, then shaking the plastic bottles at 200 rpm (25 °C) for certain periods of time in the thermostatic water bath shaker. Then, at each interval, the solution was filtered through Whatman filter paper No 1. Then, in each sample, 2 mL of 0.5 M H_2SO_4 and 1 mL of diphenyl carbazide solutions were added and allowed to stand for 10-15 min until full-color red violet was formed. Using a double beam UV-Visible spectrophotometer at a wavelength of 540 nm, the residual Cr(VI) ions left in the filtrate were analyzed. The equilibrium time was determined at a time with the highest adsorption efficiency of Cr(VI).

3.5.2. Effect of pH

Experiments were performed for each adsorbent at pH 1, 2, 3, 4, 6, 8, 10 and 12 to study the effects of pH on the adsorption mechanism and to establish the optimum pH by contacting 0.1 g of both sorbents and 40 mL of 5 mg/L of Cr(VI) working solution in plastic bottles. The solution's pH was modified by the drop wise addition of 0.1 M HCl and NaOH to the desired value. Until the adsorbents in the solution are applied. The bottles containing the mixture were left in a shaker for a thermostatic water bath and shaken for equilibrium time at 200 rpm at 25 °C. The bottles were removed from the thermostatic water bath shaker when the equilibrium time

for adsorption was done and filtered by Whatman filter paper No 1. The residual Cr(VI) ions left in the filtrate were analyzed with 1,5 diphenyl carbazide reagent and 2 mL of 0.5 M H_2SO_4 by double-beam UV-Visible at 540 nm. The optimal pH with the highest adsorption efficiency of Cr(VI) was calculated by pH [48].

3.5.3. Effect of initial concentration

The effect of initial Cr(VI) concentrations on the adsorption efficiency was tested at 40 mL of Cr(VI) with different initial chromium concentrations of 1-80 mg/L for both Tella residue and pea (*P. sativum*) seed shell at optimum contact time, pH, adsorbent dose (0.1 g), shaking speed 200 rpm, and 25 °C temperature. After the equilibrium time of adsorption has been completed, the adsorbent was extracted from each solution by filtration after the adsorption equilibrium time was completed and the concentration of residual Cr(VI) ions remaining in each solution was analyzed by a double beam UV-Visible spectrophotometer using the DPC method at a wave length of 540 nm.

3.5.4. Adsorption cycle

The experiments for each adsorbent were carried out using 0.1 g adsorbent in 40 mL of 5 mg/L working solution in plastic bottles under optimal pH, time, initial concentration and temperature conditions. The bottles containing the mixture were left in a shaker in the thermostatic water bath and shaken for equilibrium time at 25 °C by 200 rpm. The bottles were removed from the thermostatic water bath shaker when the equilibrium period for adsorption was done, and filtered by Whatman filter paper No 1. The residual Cr(VI) ions left in the filtrate were analyzed with 1,5 diphenyl carbazide reagent and 2 mL of 0.5 M H_2SO_4 by double-beam UV-Visible at 540 nm. The optimal pH with the highest adsorption efficiency of Cr(VI) was calculated by pH.

3.5.5. Data analysis

3.5.5.1. Adsorption Kinetics

It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process were evaluated. The biosorbents(Tella residue and Pea(*P. sativum*)seed shell were collected from the polyethylene bottle after 1-720 min and filtered, the filtrate were analyzed for chromium concentrations followed the colorimetric methods at optimum chromium concentration, pH, adsorbent dosage and agitation speed[73]. The experimental data was evaluated using non-linear form of pseudo-first-order and pseudo-second-order kinetics are given in equations (10) and (11), respectively.

$$q_t = q_e \left(1 - \exp^{-K_1 t}\right) \tag{10}$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \tag{11}$$

$$V_0 = K_2 q_e^2 \tag{12}$$

Where, Vo is Adsorption affinity, k_1 (min^{-1}) is pseudo-first-order rate constant, k_2 (g mg^{-1} min^{-1}) is pseudo-second-order rate constant, q_t and q_e are the adsorption capacity (mg/g) at any time t (min) and at equilibrium, respectively.

To predict the potential rate-limiting steps in the adsorption processes, intra-particle diffusion models (Webere Morris model) [54] ,was also used (Eq. 12) to analyze adsorption kinetics data.

$$q_t = k_p t^{0.5} + c \tag{13}$$

Where, q_t is the amount of Cr(VI) adsorbed on the adsorbents (mg/g) at time t, k_p (mg/(g.min$^{0.5}$)) is the intra-particle diffusion rate constant; and c (mg/g) is the intercept of the intra-particle diffusion model. If the rate-limiting step of Cr(VI) removal is the intra-particle diffusion, the plot of q_t against the $t^{1/2}$ should be a straight line and pass through the origin[74].

3.5.5.2. Adsorption Isotherms

Adsorption isotherm study was carried out by fitting the equilibrium data to two isotherm models: the Langmuir and Freundlich isotherm models. The study of isotherms was carried out by

varying the concentration of metal ion solution (1, 2,7.5, 10, 15, 20,25, 30, 40 50 ,60, 70, and 80 mg/L) but keeping the other parameters constant like volume (mL), dosage of adsorbent (g), pH, contact time interval, and temperature (25 °C). The adsorption equilibrium data were analyzed in terms of the Freundlich and Langmuir isotherm models.

I.   Langmuir isotherm model

The non -linear form of Langmuir isotherm equation could be written as

$$q_e = \frac{Q_{max}bC_e}{(1 + bC_e)} \hspace{4cm} (14)$$

Where q_e (mg/g) are the amount of Cr(VI) adsorbed per unit mass of sorbent) Ce (mg/L) is equilibrium concentration in solution or unabsorbed Cr(VI) concentration in solution (mg/L), Q_{max} (mg/g) is the maximum adsorption capacity based on the Langmuir equation; and b (L/mg) is the Langmuir constant [75].

The important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor (R_L), which is defined as in Eq. 14.

$$R_L = \frac{1}{1 + bC_0} \hspace{4cm} (15)$$

Where, C_o (mg/L) is the initial Cr(VI) concentration; and b (L/mg) is the Langmuir constant. The R_L values indicate the type of adsorption as either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$), or irreversible ($R_L=0$) [76].

II.   Freundlich isotherm model

The Freundlich equation could be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, 1/n reflects the curvature

in the isotherm and may represent the energy distribution of adsorption sites. The non-linear form of Freundlich adsorption isotherm

$$q_e = K_F C_e^{1/n} \tag{16}$$

Where, q_e (mg/g) is the equilibrium adsorption capacity; K_F ($mg^{1-1/n}$ $L^{1/n}$/g) is the adsorption coefficient based on the Freundlich equation; $1/n$ is the adsorption intensity based on the Freundlich equation.

3.5.5.3. Statistic test

Besides the coefficient of determination, the nonlinear chi-square (χ^2) statistic test was used to identify the best model fit to the observed experimental data. The χ^2 is computed using Eq. (16) as described by [77].

$$\chi^2 = \sum (q_e - q_{e,cal})^2 / q_{e,cal} \tag{17}$$

where $q_{e,cal}$ is the equilibrium adsorption capacity calculated from the model; and q_e is the experimental equilibrium adsorption capacity.

3.6 Quality control

In order to determine the accuracy of the data collected, all batch tests were recorded in triplicate and by using control in each experiment. All polyethylene bottles and lab items were washed with detergent, followed by repeated rinse with distilled water and soaked overnight in 10% HNO_3 for 24 hours, then rinsed three times with distilled water and dried.

Experimental analyses were carried out using chromium containing a working solution prepared from intermediate solution. The experiments confirm that the initial chromium concentration, pH and Cr(VI) ratio changed during the experiment because of the interaction between adsorbent and adsorbate. The accuracy of the analytical techniques was verified by using control.

Regression and chi-square analyses of experimental data were performed using Origin 8 software. The correlation coefficient (R^2) and standard error in the evaluation of parameters were studied to characterize the accuracy of the optimal analysis of the data fit.

4. Results and Discussion

In these batch adsorption studies, a variety of parameters such as effect of contact time, pH, and initial concentration were investigated to determine the effectiveness of the adsorbent in the removal of Cr(VI) from the aqueous solution. The data obtained from these studied were fitted to the common adsorption models, so that to assess the kinetics and thermodynamic behavior of the adsorption of Cr(VI) on Tella residue and Pea (*P. sativum*) seed shell. Preliminary study and adsorbent characterization have also been performed.

4.1. Screening of adsorbents

There were eleven locally available adsorbents collected from Jimma City for chromate selective adsorption testing. The hexavalent chromium adsorption properties of these locally accessible adsorbents have been investigated. Most adsorbents, with the exception of ash and egg shells, have a reasonable removal efficiency of Cr(VI). Two of the eleven overall adsorbents (Tella residue and Pea (P. sativum) seed shell) were selected based on the preliminary test results and also they were not investigated previously for removal of chromium from aqueous solution.

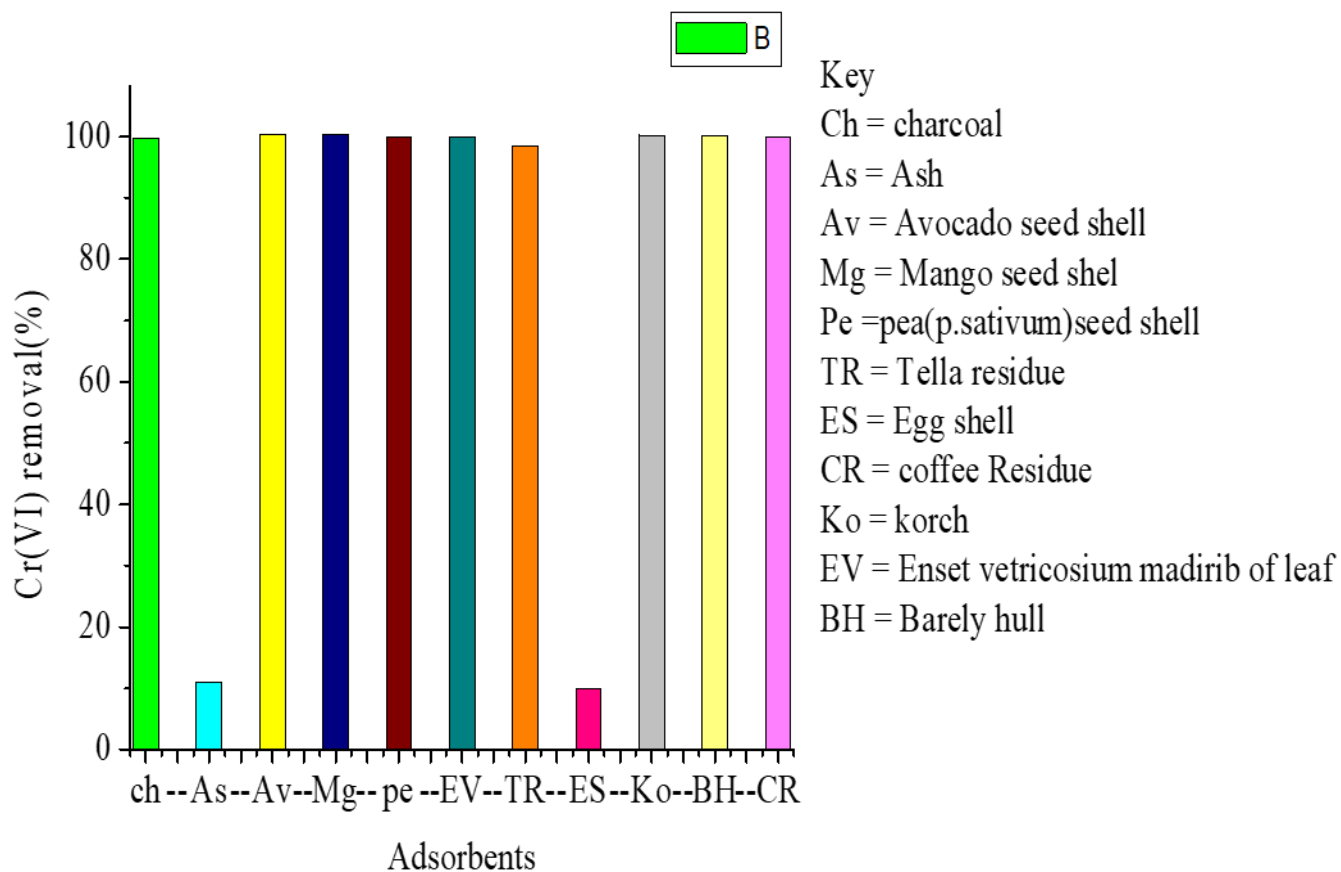**Figure 1** Screening of adsorbents: initial Cr(VI) concentration (5 mg/L), 2.5 g/L adsorbent dose, pH 2, contact time 24 h, shaking speed 200 rpm, at 25 °C

4.2 Characterization of adsorbent

4.2.1 Physicochemical properties of adsorbent

The physicochemical properties of the adsorbents such as pH, moisture contents, ash, volatility, surface area, and dry matter were investigated and the obtained results are shown in Table 3.

Table 3 physiochemical properties of adsorbents

Parameter	Tella residue	Pea (*P. sativum*) seed shell
Moisture content %	6.70	10.00
Dry mater %	93.30	90.00
Ash %	14.78	14.92
Volatile	12.00	13.18
Fixed carbon	66.52	61.90
Surface area(m^2/g)	59.26	132.60
pH	3.27	6.12

Moisture content is one of the important features that reflects the adsorbent quality. The moisture content of Tella residue and Pea (*P. sativum*) seed shell were found to be 6.7% and 10% respectively. Which is lower as compared to other adsorbents such as activated carbon from coffee husk which has the moisture content of 19% [39]. whereas the dry matter content of both samples was 93.3% and 90%, respectively (**Table 3**). The moisture content of a sample refers to the percentage of water content of the sample. The lower the moisture content, the higher its adsorption efficiency since water molecules can have the potential effect in the pores of an adsorbent through filling the adsorbent binding site before it contacts with the solution. Therefore, adsorption efficiency decrease with an increase in moisture content of an adsorbent [78].

The ash content is a measure of total amount of inorganic compounds such as minerals in the adsorbents. It can influence the adsorptive capacity of the adsorbents as it is linked directly to the pore structure even if the effect is negative [79]. The percentage of ash content for pea (*P. sativum*) seed shell and Tella residue samples were found to be 14.92% and 14.78%, respectively. The obtained values for both sorbents were favorable during the adsorption. The lower the material's ash content, the better it is to be used as an adsorbent. Volatile matter is associated to the residual organic compounds in the prepared adsorbent. The obtained volatile matter for Tella residue and Pea (*P. sativum*) seed shell were 12.00% and 13.18%, respectively. The fixed carbon is the solid combustible residue that remains after the sample was heated and the volatile matter was expelled. Fixed carbon was the combustible residue left after removing the moisture content,

volatile matter and ash from the sample and its value were 66.52 and 61.90% for both sorbents respectively.

Specific surface area of Tella residue and pea (*Pisum sativum*) seed shell were 59.26 and 132. 60 m^2/g respectively which indicates that the adsorbent surface is good for adsorption process Pea (P. sativum) seed shell is better adsorbent than Tella residue because of high surface area and porosity.

4.2.2. Point of zero charge

The point of zero charge is the pH value at which the surface charge of an adsorbent equals to zero. The experimental results of pHpzc of Tella residue was 4.5 and pea (*P. sativum*) seed shell was found to be 6 in this study as shown in the **Figure 2**
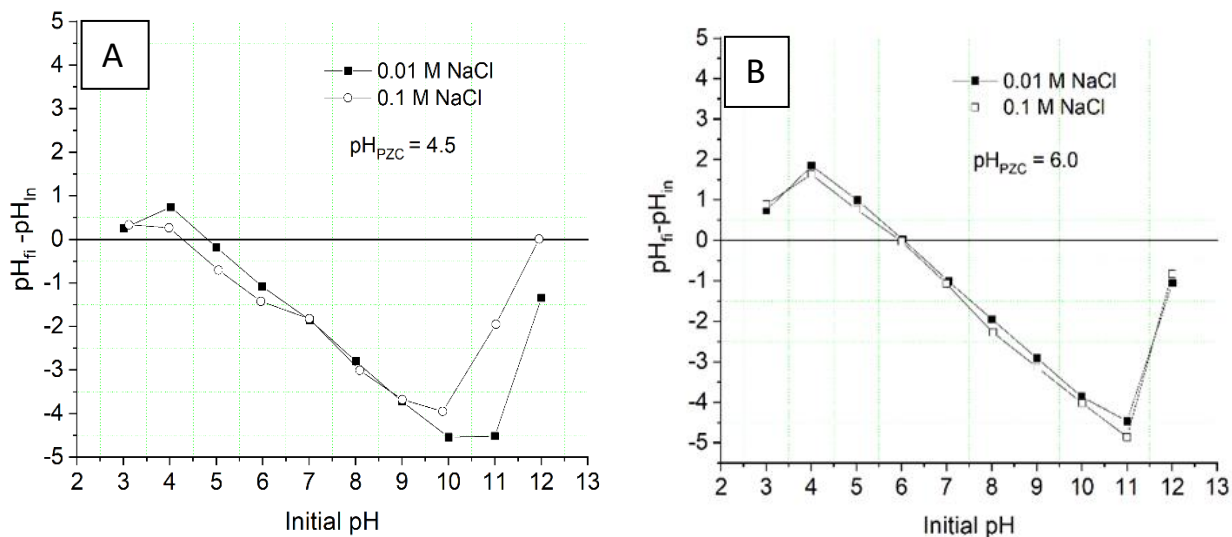
Figure 2 Determination of pHpzc: (A) Tella residue and (B) Pea (*P. sativum*) seed shell

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pHpzc) of the adsorbent because the point of zero charge is the pH value at which the surface charge of an adsorbent equals to zero. When the pH of the aqueous solution is below the pHzpc, the surface of the adsorbent will become positively charged and anion adsorption happens due

to electrostatic interaction of anions with the positively charged surface of the adsorbent. However, the surface of the adsorbent will become negatively charged when the solution pH is greater than zero point of charges. The relationship between pHpzc and adsorbent capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the pHpzc while anions adsorption will be favorable at pH values lower than the pHpzc. The pH of the solution affects the surface charge of the adsorbents as well as the degree of the ionization and speciation of different pollutants. Change in the pH affects the adsorptive process through dissociation of functional groups as the active sites on the surface of the adsorbent. This subsequently leads to a shift in the reaction kinetics and the equilibrium characteristics of the adsorption process. Adsorption of the various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to deposition of OH^- ions [80].

4.2.3. FT-IR analysis of adsorbent

The functional groups of Tella residue and Pea (*P. sativum*) seed shell were studied by using FT-IR spectroscopy as shown in **fig 3** below.

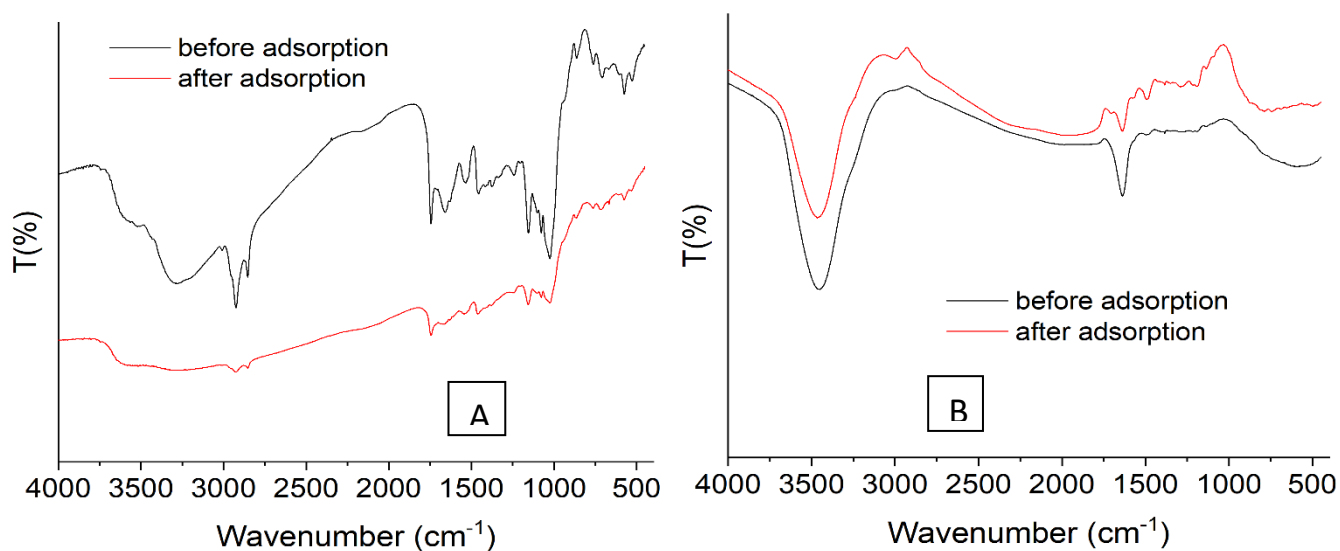**Figure 3** FT-IR analysis of adsorbent surface (A) (Tella residue) and (B) *Pisum sativum* seed shell before and after adsorption

The FT-IR spectra were recorded before and after sorption of chromium to determine the vibrational frequency changes (if any) for the functional groups in the adsorbents. The FT-IR spectra, the region 3500-3150 cm^{-1} is assigned as OH stretching in the Tella residue (**figure 3 A& B**). The intense band on the region from 3000-2800cm^{-1} C-H$_3$ (SP^3) stretching of alkane functional group. The (CH$_{3)}$ sp3 peak is shifted to 2927-2933cm^{-1} when Cr(VI) is adsorbed. The small intense band at 2900-2645 cm^{-1} indicate the presence of C-H$_2$ stretching, and The region between 1470-1450 cm^{-1} shows C-H bending and the region between 1250-1020 cm^{-1} shows NH$_2$ (secondary amine) and 1050 indicates C-O stretching.

The functional groups of Pea (*P. sativum*) seed shell were studied before and after adsorption by using FT-IR spectroscopy. The region from 3500-3250 cm^{-1}sharp intense peak indicate primary NH group and small intense peak 3000-2800 cm^{-1} indicates (CH$_3$) sp3-carbon. The (CH$_{3)}$ sp3 peak is shifted to 2927-2933cm^{-1} when Cr(VI) is adsorbed. The medium peaks at 1680-1640 cm^{-1} indicate C=C stretching of alkenes. In general, **Figure 3 A & B** shows that changes in shape and shift in peak position were observed in the FT-IR spectra following adsorption of Cr(VI) as a result of the functional group participating in the process of metal binding or adsorption and the adsorbent surface occupied by metal ions.

4.2.4. XRD Analysis of Adsorbent

XRD diffraction is the tool, which have been used in order to understand the transformation of amorphous to crystalline of adsorbent if the interaction between adsorbent and adsorbate took place. The XRD pattern for both adsorbents (Tella residue and pea (*P. sativum*) seed shell) and adsorbents loaded with Cr(VI) ions is shown in **Figure 4 A & B.**
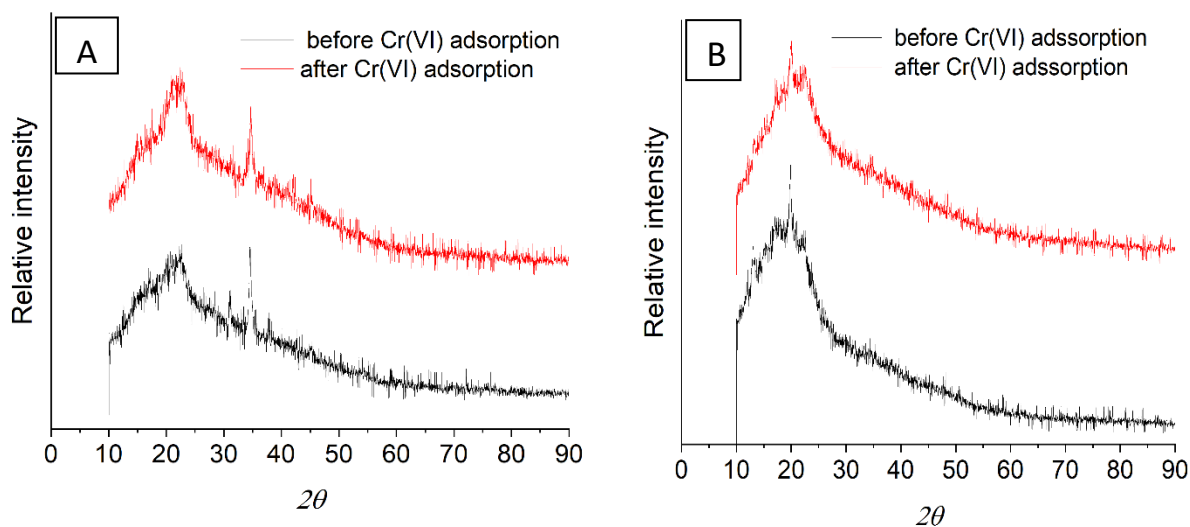
Figure 4 XRD data of (A) (*P. sativum*) seed shell and (B) Tella residue before and after adsorption

The XRD studies, indicates that there was no change   the adsorbents loaded with Cr(VI) ion and unloaded Cr(VI) ion The presence of an amorphous phase in the sample can lead to an irregular noise base line. Therefore, the XRD studies provide information about only amorphous nature of bio adsorbents.

4.3. Adsorption of Cr(VI)

4.3.1. Effect of contact time

The effect of agitation time is one of the important parameters on the percentage removal of Cr(VI) ions by the adsorption of both Tella residue and Pea (*P. sativum*) seed shell to establish adsorption kinetics. In other words, the percentage removal of Cr(VI) ions depends on contact time. The time dependency of Cr(VI) adsorption on both Tella residue and pea (*P. sativum*) seed shell adsorbents was investigated by varying the contact time in the range of 5 min to 12 h and 1 min to 2 h, respectively. While the effect of other parameters, like pH, adsorbent dosage, and initial Cr(VI) concentration, were kept constant. The effect of contact time on Cr(VI) adsorption efficiency is shown in **Figure.5 A & B**,
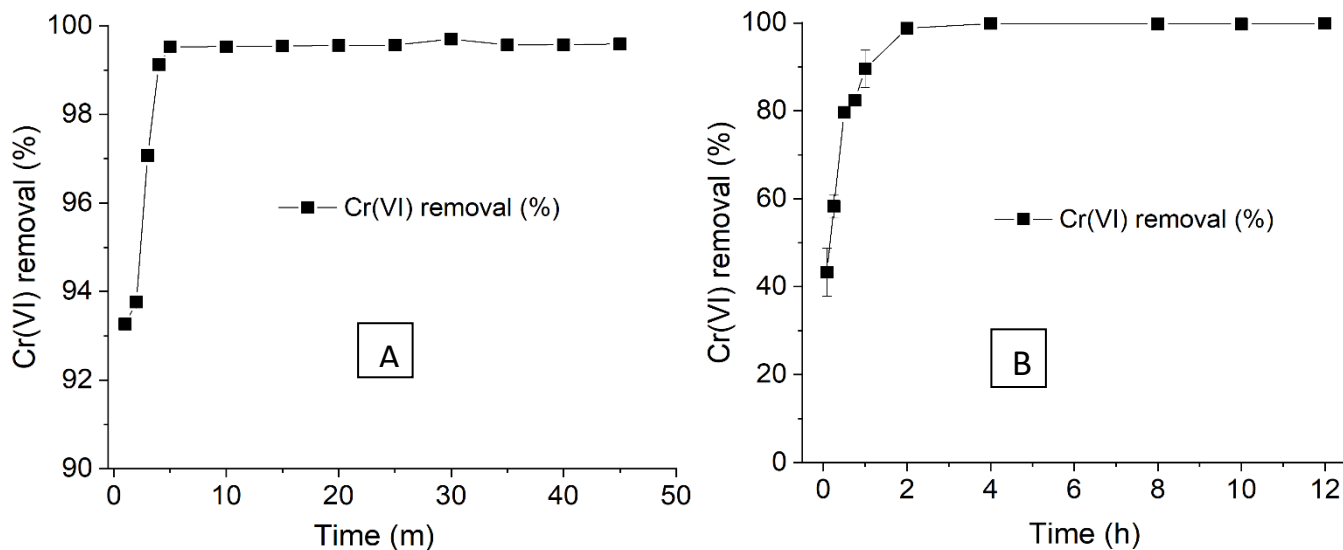
Figure 5 Effect of contact time on the Cr(VI) removal by (A) Pea (Pisum sativum) seed shell and (B)) Tella residue adsorbents at Cr(VI) of 5 mg/L, adsorbent dosage, 2.5 g/L, shaking speed 200 rpm, temperature 25 °C, and pH 2

As indicated in **figure (5)** the Cr(VI) removal efficiency increases with increasing contact time. Approximately 43-99% and 93-99% of Cr(VI) Tella residue and pea (*P. sativum*) seed shell adsorbents. Maximum percentage of adsorption occurred after 2h for Tella residue and 10 min for Pea (*P. sativum*) seed shell adsorbents, and then it becomes almost remained constant for each of the adsorbent. Therefore, 4 and 1 h were considered as equilibrium time for Tella residue and Pea (*P. sativum*) seed shell adsorbents, respectively. Initially, the adsorption rate increased rapidly by increasing the contact time due to the large number of vacancies on the adsorbent surface to absorb metal ions. With rising contact time, Cr(VI) ion adsorption has increased. This is due to prolonged interaction with the adsorbate (chromium ion) between the sorbent surface and can be related to the increased intra-particle diffusion that occurred during longevity. This can be explained by the fact that a large number of vacant surface sites may initially have a high concentration gradient for Cr(VI) ion adsorption, and the surface sites will become depleted by time. Upon depletion of active adsorbent sites, the rate of absorption is controlled by the rate at which the adsorbate is transferred from the outside to the inside when

balance is reached. Therefore, for further studies of adsorption with other variable parameters the optimum time of 4 and 1 h, respectively for Cr(VI) adsorption were chosen as equilibrium time.

4.3.2 Effect of pH

The pH of the solution plays an important role in the control of the surface charge of the adsorbent and the removal of the adsorbate (metal ion) from the solution. Hence it becomes necessary to determine at what pH, maximum adsorption can take place. The effect of pH of Cr(VI) solution was investigated in the pH range from 1-12 for Tella residue and Pea (*P. sativum*) seed shell adsorbents using a fixed mass (0.1 g) of the adsorbent in 40 mL of 5 mg/L Cr(VI) solution shaking for 4 and 1 h, respectively. The experimental data indicates that the adsorption capacity and percentage removal of Cr(VI) increase with decrease in initial pH values (pH < pHzpc) the surface charge of the adsorbent may get positively charged as result of being surrounded by H^+ ion in solution which enhance negatively charged Cr(VI) adsorption through electrostatic forces of attraction. (**Figure 6 A &B**). With increase in pH (pH > pHzpc), is possibly because the surface of sorbents acquire negative charge as the solution pH increased, thus result in the electrostatic repulsions with Cr(VI) ions [81].
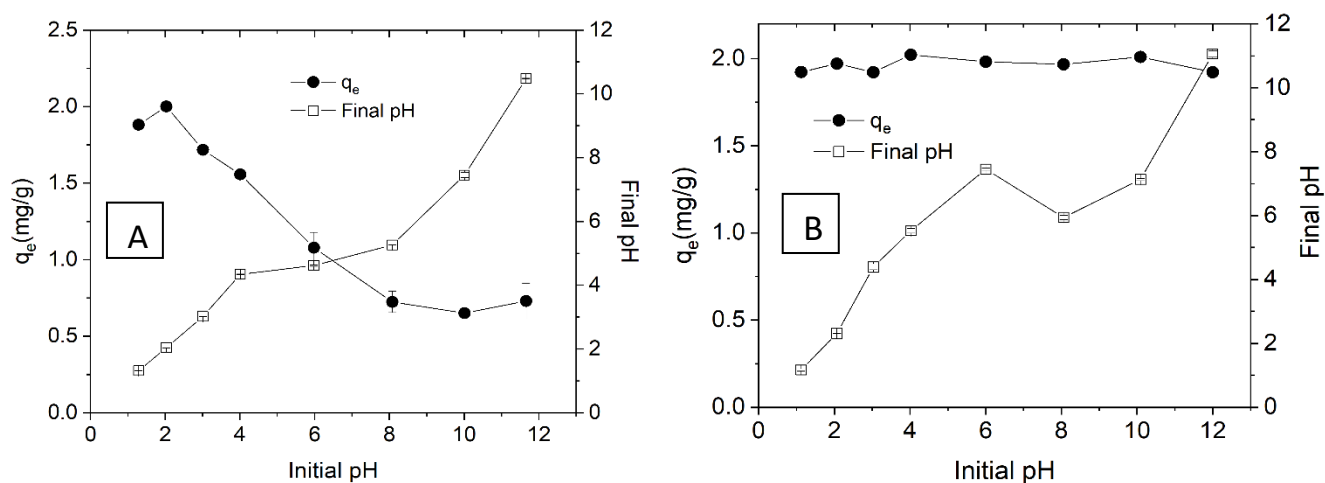

Figure 6 Effect of pH on the absorption of Cr(VI) onto (A) Tella residue and (B) pea (*Pisum sativum*); initial concentration of Cr(VI) 5 mg/L, shaking speed 200 rpm, adsorbent dose 2.5 g/L and temperature25 °C

In acidic environment, the main chromium species are hydrogen chromate ($HCrO_4^-$), Chromate ($Cr_2O_7^{2-}$) and Chromic acid (H_2CrO_4), while in alkaline medium monochromate (CrO_4^{2-}) predominates. In acidic solution, the adsorbent surface was protonated to a high extent(the surface charge of adsorbent is positive at low pH, and this may promote the binding of the negatively charged $HCrO_4^-$ ions[82]. The equation (20) below shows $HCrO_4^-$ species are easily exchanged with OH^- at active surfaces of adsorbent under acidic conditions.

$$Ar\ OH + HCrO_4^- + H^+ \rightarrow ArHCrO_4 + H_2O \qquad (20)$$
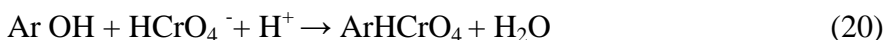
Where, Ar is surface charge of adsorbent[83].

The decrease of the sorption with increasing pH could be attributable to the decrease of electrostatic attraction and competition between bulk chromium anionic species ($HCrO_4^-$ and CrO_4^{2-} and OH^- ions for adsorption at active sorbent sites[84]. As pH increased, abundance of OH^- ions on the adsorbent surface caused repulsive force between adsorbent and adsorbate in the solid- liquid phase, which resulted in a reduction of the adsorption. Metal sorption capacity is highly pH dependent. Solution pH influences the metal species and adsorbent surface charge. Therefore, metal sorption capacity is dependent upon the adsorbent type, the metal species and the pH of solution. In view of these observations, the value of pH 2 and 3 was taken as the optimum pH for further experimental studies for Tella residue and Pea (*P. sativum*) seed shell, respectively.

4.3.3 Effect of Initial Chromium (VI) Concentration

The effect of the initial concentration of Cr(VI) adsorption on Tella residue and Pea (*P. sativum*) seed shell was investigated. The concentrations of 1- 80 mg/L for both Tella residue and pea (*Pisum sativum*) seed shell at contact time of 4 and 1 h, pH 2 and 3, adsorbent dosage of 0.1 g and temperature of 25 °C. The obtained results are shown in **Figure 7.**
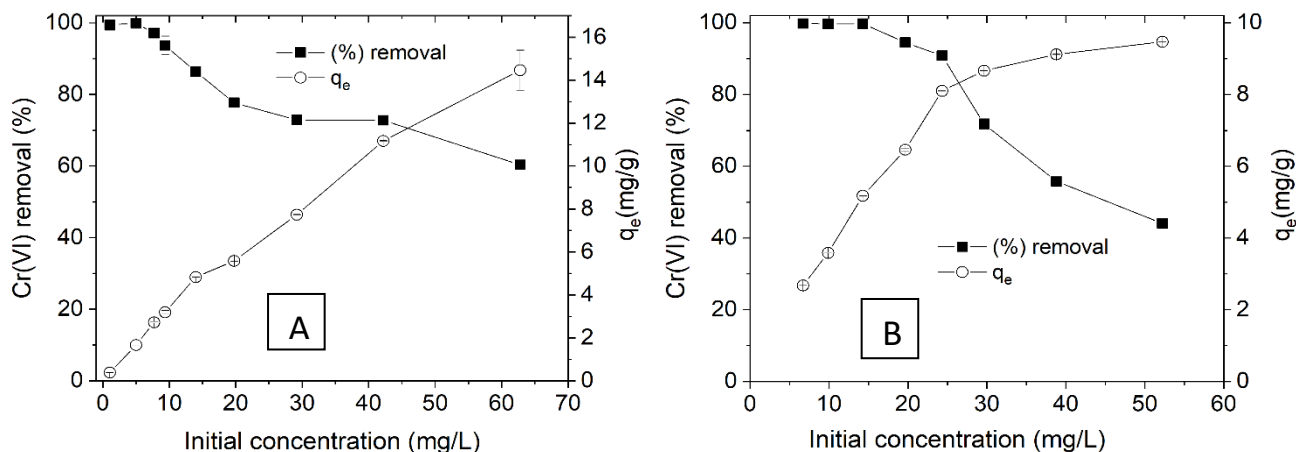
Figure 7 Effect of initial concentrations on adsorption of Cr(VI) onto (A) Tella residue and (B) Pea (*P. sativum*) seed shell at optimum pH, shaking speed 200 rpm, adsorbent dose 2.5 g/L, and temperature 25 °C

As shown in **Figure 7**, the percent removal of Cr(VI) from the solution decreased with an increase in the initial Cr(VI) concentration from 1 to 80 mg/L. This is due to the fact that at a lower concentration, there were enough active sites that adsorbents could easily take up. However, at higher concentrations, insufficient surface area to allow a much greater presence of Cr(VI) ions in the solution. This could be caused by the limited adsorption sites of Tella residue and pea (*P. sativum*) seed waste for adsorption of Cr(VI) ions. Therefore, Cr(VI) ions have not been fully adsorbed from solutions due to saturation of linkage sites[81], [85]. Furthermore, electrostatic repulsion between negative loads of adsorbed ions leads to a decrease in adsorption percentages, which is consistent with other work[86]. The adsorption capacity of Cr(VI) ions on Tella residue and pea (*P. sativum*) seed shell adsorbents increases from 5.5 to 15.6 mg/g and 2.7 to 8.5, respectively when Cr(VI) ion concentration is increased. This due to high driving force for mass transfer at higher initial concentration of Cr(VI) ion [87].

4.3.4 Adsorption Kinetic studies

In order to evaluate the adsorption kinetics, the experimental data was evaluated using non-linear form of pseudo-first-order and pseudo-second-order kinetics are given in equations (10) and (11), respectively. This is because of non-linear regression method is more appropriate compared

to linear method to determine the rate kinetic parameters[88]. Pseudo-first-order and pseudo-second-order models were tested to analyze the adsorption kinetics. Both adsorption kinetic models have been used to understand the adsorption kinetics and the correlation coefficient (R^2) and chi-square (χ^2) were compared to determine the better fitted model. However, the correlation coefficient, R^2, values showed that the pseudo-second-order model fits better for both adsorbents to the experimental data than the pseudo-first order model (**Fig 8 and Table (4).** Here, the observed rate constant (k_2,) was considerably greater than with some reported value for chromium adsorption on the variety of adsorbents [89], [90], [86] , which indicate that the Tella residue and *P. sativum* was an efficient adsorbent for Cr(VI) removal from aqueous solutions. Thus, the batch adsorption experiment of removal Cr(VI) by using Tella residue and pea (*P. sativum*) adsorbents follows pseudo-second-order kinetic model.
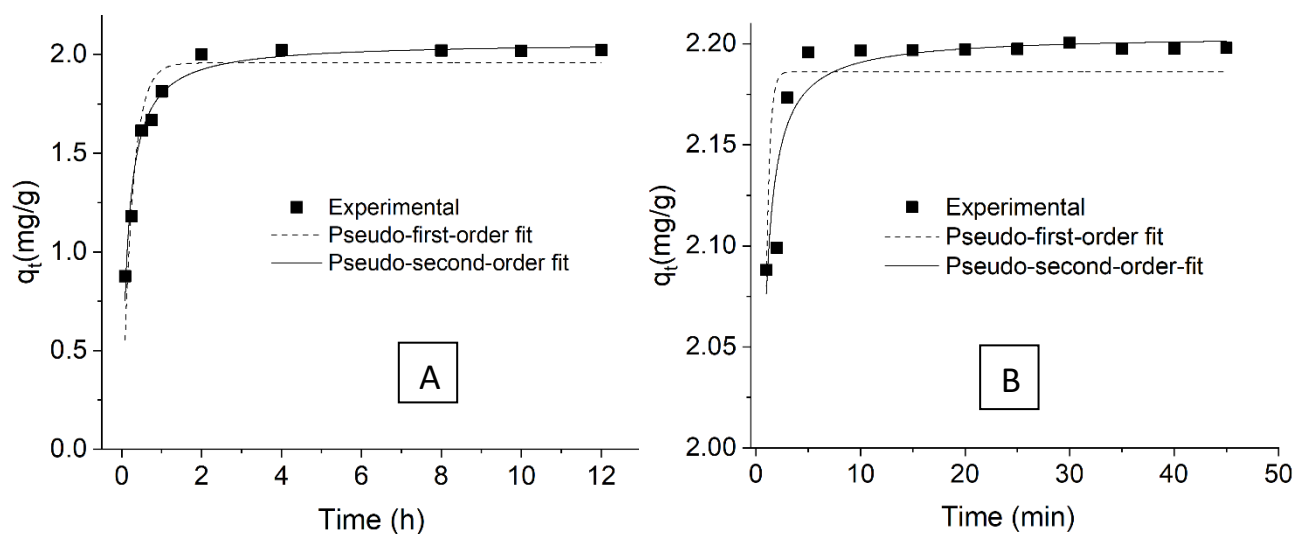

Figure 8 Pseudo second order (PSO) and pseudo first order (PFO) plot for adsorption of Cr(VI) onto (A) Tella residue and (B) pea (*Pisum sativum*) seed shell

Table 4 Parameters of the pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) adsorption by Tella residue and Pea (*P. sativum*) seed shell

Parameter	Tella residue		Pea seed shell	
	PFO	PSO	PFO	PSO
C_o(mg/L)	5	5	5	5
$q_{e,exp}$(mg/g)	2.0224	2.0224	2.1980	2.1980
$q_{e,cal}$(mg/g)	1.958	2.0635	2.1876	2.2044
k_1(min^{-1})	3.979	-	3.010	-
k_2(g/(mg.min))	-	3.349	-	7.358
V_0(mg/(g.min))	-	14.26	-	35.76
R^2	0.8774	0.9710	0.5457	0.8727
χ^2	0.0225	0.00532	8.08×10^{-4}	2.26×10^{-4}

The values of $q_{e,cal}$ (calculated) and $q_{e,exp}$ (experimental) are similar for each adsorbent. The value of R^2 for the pseudo-first-order model was not satisfactory except for Tella residue, but the pseudo-second-order-kinetic model exhibited overall high R^2 and low χ^2 values (**Table 4.).** Therefore, it can be concluded that the pseudo-second-order kinetic model is more suitable to describe the adsorption kinetics of Cr(VI) on Tella residue and Pea(*P. sativum*) seed shell.

Adsorption affinity provides information on the adsorption rate at the beginning of the adsorption process. The calculated value of V_0 for Pea seed shell and Tella residue indicates that the adsorption of Pea (*P. sativum*) seed shell was about 2.5 times faster than that of Tella residue. However, the pseudo-second-order model has an inherent limitation by assuming the adsorption phenomenon as a single, one-step binding process, although the adsorption process proceeds in three steps, namely, external surface diffusion, intra-particle diffusion, and finally adsorption. Each of these steps could be rate-determining. Since the adsorption was carried out in a well-agitated system, external diffusion resistance could be quite small and intra-particle diffusion could be the rate-determining step. Therefore, the adsorption kinetics were examined by applying the Weber and Morris intra-particle diffusion model [74] that is given by (Eq. (13)) in section 3. **Fig. 9** shows plots the intra-particle diffusion model of experimental data.
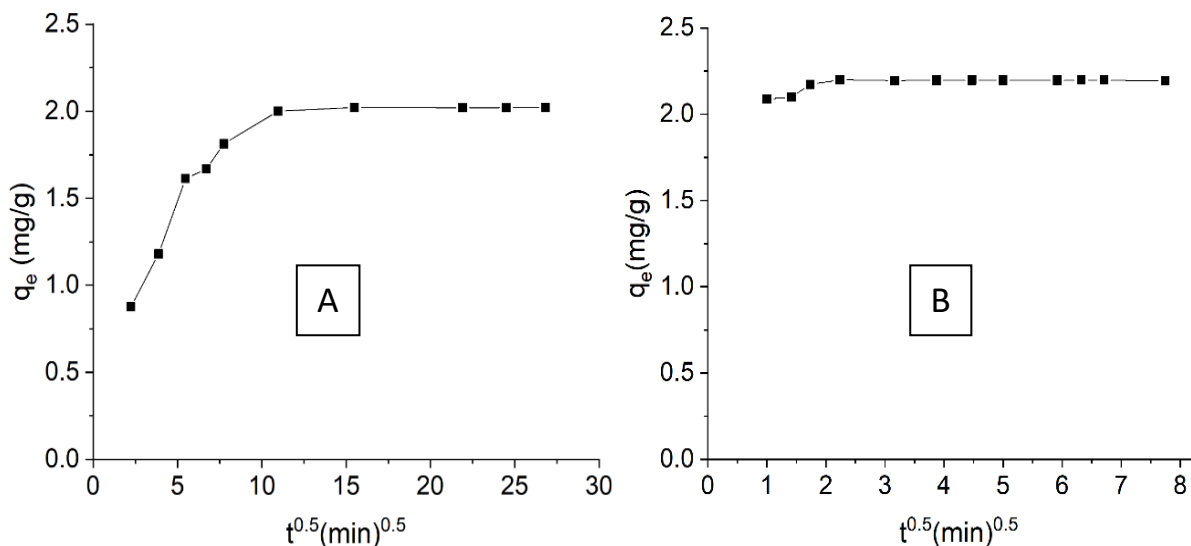
Figure 9 Intra-particle diffusion plots of Cr (VI) adsorption on (A) Tella residue and (B) pea (*P. sativum*) seed shell

It is clear that each curve shows a multi-linear plot (**Fig 9A and B**). However, each curve does not pass through the origin which indicates that intra-particle diffusion was not the only rate-determining step. Therefore, the adsorption of Cr(VI) and its kinetics could be the overall effect of the external diffusion transport of Cr(VI), the intra-particle diffusion of the ions and the adsorption of Cr(VI) ions by the active sites on the adsorbent (Tella residue and pea (*P. sativum*) seed shell) [48] In most of the previous studies, such as adsorption of Cr(VI) onto polypyrrole-polyaniline nanofibers[91] ,Cr(VI) onto Waste of Bamboo (*Oxytenanthera abyssinica*) [92], and Cr(VI) onto Nut shell powder [93], the plots did not pass through the origin and the intra-particle diffusion was not the only rate-controlling step.

4.3.5 Adsorption Isotherm study

Adsorption isotherms are mathematical models that describe the distribution of adsorbed species among liquids and adsorbents, based on a set of assumptions mainly related to adsorbent heterogeneity/homogeneity, the type of cover and the potential for interaction between adsorbed species. Langmuir and Freundlich model are adsorption isotherms mostly used by many

researches. In this study Langmuir isotherm model and Freundlich isotherm model were used to describe the adsorption of Cr(VI) ions on to Tella residue and Pea (*P. sativum*) seed shell adsorbent using different initial Cr(VI) ions concentrations of 1, 2, 7.5, 10, 15 20, 30, 40, 50 ,60, 70, and 80 mg/L by keeping the other variables constant (volume Cr(VI) solution 40 mL, adsorbent dose 0.1 g, pH 2 &3, contact time 4 h & 1 h, and temperature 25 °C). The nonlinear forms of these models are given in equation (14) and (16), respectively. The isotherm models and the calculated constants from the experimental data are presented in **Figure 10 and Table 5.**
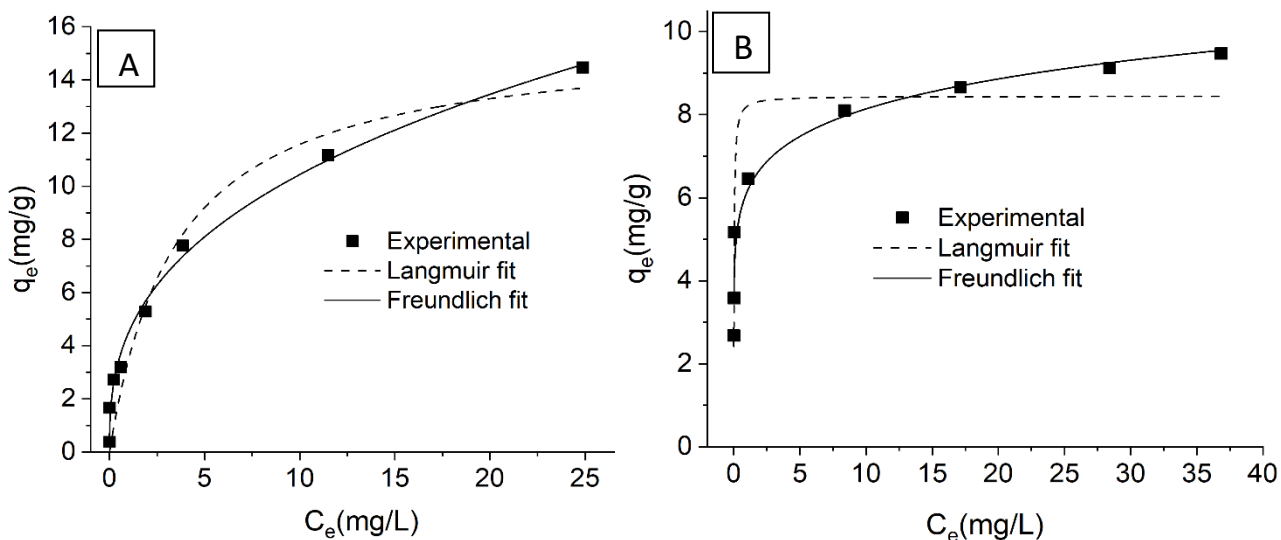
Figure 10 Langmuir and Freundlich isotherm model for the adsorption of Cr(VI) onto (A)Tella residue and (B) Pea (*Pisum sativum*) seed shell

The Langmuir model assumes that the uptake of adsorbate molecules occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules that is, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at the site[94]. From nonlinear analysis the Langmuir isotherm does not fit well the equilibrium data with weak the correlation coefficient.

RL, is the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless equilibrium parameter also known as the separation factor. In the present study, RL was found to be 0.0526-0.7665 and 0.0005-0.0277 for Tella residue and Pea (*P. sativa*) seed shell, respectively. The R_L values were in the ranges (0 < R_L < 1), which indicates favorable

adsorption of Cr(VI) on both Tella residue and Pea (*P. sativa*) seed shell adsorbents. As initial concentration increases, R_L value is closer to zero which is due to effect of pore diffusion in the adsorption process [51].

Freundlich model is suitable for non-ideal adsorption on heterogeneous surfaces. The heterogeneity is caused by the presence of different functional groups on the surface, and various adsorbent–adsorbate interactions. The Freundlich isotherm is represented by Equation (16) and k_f and n are constant incorporating all factors affecting the adsorption process. In the Freundlich equation, the heterogeneity factor (1/n) is related to the capacity and intensity of the adsorption. n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n = 1, the adsorption is linear; n < 1 this implies that adsorption process is chemical and n > 1 indicates physical process is a favorable and C_e is the equilibrium concentration (mg/L) .The value of 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface [95] .

 It is generally stated that values of sorption intensity, n in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor adsorption characteristics [96]. In the present study the value of n (n= 8.1 and 2.7) is greater than 1, indicating that the adsorption process is favorable. Moreover, the values of correlation coefficients are greater than that of the Langmuir isotherm value. Thus, the results implied that adsorption of Cr(VI) took place on heterogeneous and multilayer surface energy of both Tella residue and Pea (*P. sativum*) seed shell.   in order to determine the best isotherm that could describe adsorption process of Cr(VI), data analysis was performed using linear regression that fitness of the models is often evaluated based on the value of the correlation coefficients (R^2) while Chi-square analysis has the advantage that all isotherms were compared on the same abscissa and ordinate which could be used to determine the best fitted model for isotherm. and for the determination of a non-linear model based on standard least-square normality hypotheses[97].

The Chi-square statistic test is basically the sum of the squares of the differences between the experimental data and theoretically predicted data from models. with each squared difference divided by the corresponding data obtained by calculating from the models. If the data from the model are similar to the experimental data, $\chi 2$ will be a small number, and if they are differ; $\chi 2$

will be a large number. Therefore, the data set were analyzed using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system [77]. The $\chi 2$ values are calculated using Eq. (16) and are given in **Table 5**. Based on the values of the R^2 and the results of chi-square analysis, Cr (VI) adsorption by both Tella residue and pea (*P. sativum*) seed shell can be best described by the both isotherm model given high value of R^2 and the $\chi 2$ values of both the isotherms are comparable and hence the adsorption of chromium onto Tella residue and *P. sativum* shell both Langmuir and Freundlich isotherms. The smaller $\chi 2$ values confirm a better correspondence between experimental data and isotherm model [98]. Results indicated that the Chi-square test provided a better determination for the sets of experimental data confirmed that $\chi 2$ from non-linear model of Freundlich isotherm was found to be small (0.3283) and 0.3735 for both samples.

Table 5 Isotherm parameters of the adsorption of Cr(VI) on Tella residue and Pea (*P. sativum*) seed shell

Isotherm	Parameters	Tella residue	Pea seed shell
Langmuir	q_{max} (mg/g)	15.614	8.449
	b (L/mg)	0.2867	33.0795
	R_L	0.0526-0.7665	0.0005-0.0277
	R^2	0.9507	0.8851
	χ^2	1.4035	0.9116
Freundlich	K_F $((mg^{1-1/n}L^{1/n})/g)$	4.490	6.1407
	n	2.729	8.166
	R^2	0.9885	0.9529
	χ^2	0.3283	0.3735

4 .3.6 Possible mechanism of Cr(VI) adsorption

The mechanisms of adsorption by the adsorbents were all consistent with the PSO kinetic model, indicating the adsorption of Cr(VI) by both Tella residue and pea (*P. sativum*) seed shell occurs by chemisorption. Based on the heterogeneity of the adsorbent surface as well as physical adsorption, isothermal forms adhere to the Freundlich equation. Adsorption of Cr(VI) was

highly dependent on solution pH and strongly adsorbed Cr(VI) at acidic pH, whereas alkaline pH condition showed poor or no adsorption[66]. The adsorption capacity and percentage removal of Cr(VI) increase with decrease in initial pH values the surface charge of the adsorbent may get positively charged as result of being surrounded by H^+ on in solution which enhance negatively charged Cr(VI) adsorption through electrostatic forces of attraction. Most adsorbents contain acid functional groups that allow the possibility of a combined reduction-adsorption interaction. The adsorption of Cr(VI) is attributed to the interactions between ions in solution and complexes formed at the adsorbent surface.

4 .3.7 Cr(VI) adsorption cycles

The recycling of any adsorbent is of great importance as a cost effective process in water treatment [99]. As seen from **Figure 11 A & B** the adsorption efficiency of Cr(VI) ions was decreased first to four cycles for Pea(*P. sativum*)seed shell by increasing number of cycle whereas for Tella residue first to five cycles. This was happened due to the loading of active binding sites with Cr(VI) molecules and the ratio of competing active site decreases after each cycle. Therefore, percentage removal decrease with increasing number of adsorption cycle.
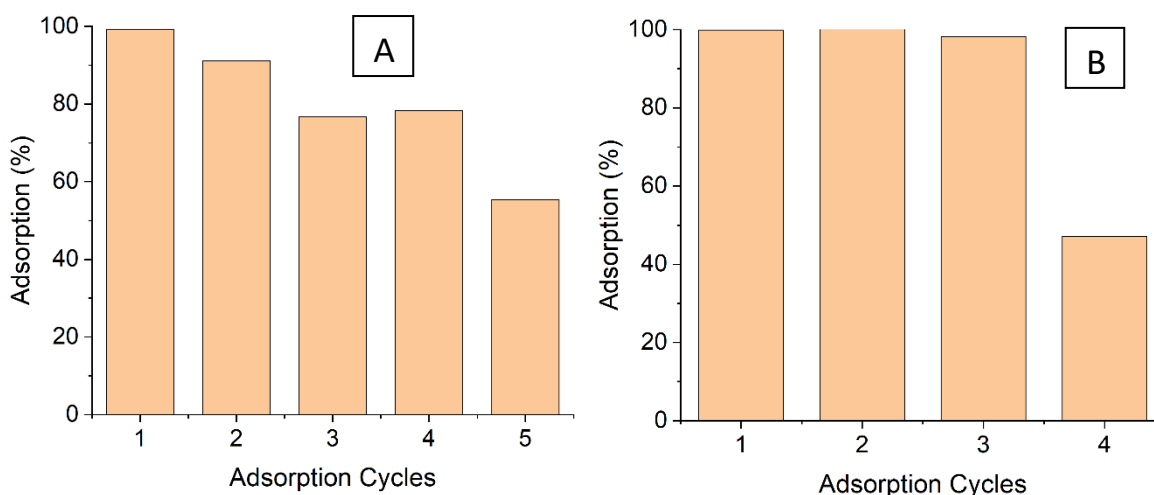

Figure 11 Cr(VI) adsorption cycle of (A) Tella residue (B) pea(*P. sativum)seed shell*

4 .3.9 Comparison of Cr(VI) adsorption with other adsorbents

The adsorptive capacity of the sorbents used in this study was compared with that of others reported in the literature and the adsorbent dose, contact time and pH values of the adsorbent capacity as shown in **Table (6)**. In the current inquiry, the experimental results were compared with recorded values. Research results of investigation showed that the adsorbents have high adsorption capacity compared to Neem leaves powder, Rice bran, wheat brane. untreated papaya peel (PP), , saw dust and powder of potato peelings Whereas paper sludge mill) , pine needle powder and Polyacrylamide modified magnetic nanoparticles are shown to have higher capacity than this work. This could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material[100]. Hence, both pea (Pisum sativum) seed shell and Tella residue can be considered to be viable adsorbent for the removal of Cr(VI) from aqueous solutions

Table 6 Comparison of adsorption capacities of Cr(VI) ion with other adsorbents reported in various studies

S/No	Adsorbent	pH	Q_m(mg/g)	Dosage (g)	Time (min)	Reference
1	Sawdust	2	0.229	0.5	160	[94]
2	Pin needle powder	3	40	0.5	45	[95]
3	Rice brane	2	0.069			[96]
4	Neem leaves powder	2	0.85	0.8	120	[97]
5	Potato powder peels	2.5	3.28	0.4	48	**[98]**
6	Untreated papaya peel	1	7.16	0.5	160	[99]
7	Wheat brane	3	0.942	0.2	60	[100]
8	Paper mill sludge	4	23.18	1	180	[101]
9	Polyacrylamide modified magnetic nanoparticles	3	35.186	0.05	40	[102]
10	Tella residue	2	15.6	0.1	240	This study
11	Pea (*P. sativum*) seed shell	3	8.5	0.1	60	This study

5 Conclusion

In this analysis, the obtained results showed that the locally available adsorbents (Tella residue and pea (*P. sativum*) seed shell are efficient for removing Cr(VI) with an efficiency of 98.43 percent within 240 minutes and 99.88 percent within 60 minutes respectively at the initial concentration of 5 mg/L of pH 2 and 3. It was found that adsorption was based on contact time, solution pH and concentrations. The FT-IR analysis of both samples before and after adsorption experiment was analyzed in order to know functional groups present on the surface of samples. In both samples the presence of alcohol, amine, alkane and alkene were confirmed by FT-IR analysis. The X-ray diffraction pictures of unloaded and loaded Cr(VI) adsorption of the Tella residue and pea (*P. sativum*) seed shell indicate that an amorphous structure. The equilibrium data using the isotherm of both the Langmuir and Freundlich and the rate of kinetics (first and second-order kinetic) models of Cr(VI) adsorption on the both samples were analyzed successfully. The adsorption data was better fitted by the Freundlich model adsorption isotherm followed by the Langmuir isotherm model over the concentration range studied and suggested that the surface is relatively heterogeneous surface energy in terms of functional groups. The second-order kinetic models provided better fit for the Cr(VI) adsorption rate for both samples. Based on the experimental data provided in this thesis work, generally. The ability to adsorb Cr(VI) ions from aqueous solution is Tella residue and pea (Pisum sativum) seed shell adsorbent. These adsorbents are also able to eliminate Cr(VI) from industrial waste water. It can be concluded that both adsorbents are used as a low-cost, effective and alternative adsorbent for the removal Cr(VI) from aqueous solution.

6 Recommendations

Tella residue and pea (*P. sativum*) seed shell had been shown in this thesis work to have the potential in removing Cr(VI) ions from aqueous solution. Further studies can be carried out by chemically and physically activating this adsorbent for chromium removal and other heavy metals, inorganic and organic chemicals like dyes and pesticides. It is also possible to study column and pilot scale for removal of Cr(VI) from real wastewater sample and in treatment of wastewater in practical applications.

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