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REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION USING ACTIVATED TARO RESIDUE CARBON AS AN ADSORBENT

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December, 2021

JU, Ethiopia

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A THESIS SUBMITTED TO JIMMA UNIVERSITY, COLLEGE OF NATURAL SCIENCE, DEPARTMENT OF CHEMISTRY IN THE PARTIAL FULFILLMENT FOR THE REQUIREMENT OF MASTER OF SCIENCE IN CHEMISTRY (ANALYTICAL)

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SCHOOL OF GRADUATE STUDENT
JIMMA UNIVERSITY
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MSc THESIS APPROVAL SHEET

We, the undersigned, member of the board of examiners of the final defense by Zelalem Desta Haile have read and evaluated his/her thesis entitled, **"Removal of Hexavalent Chromium from Aqueous Solution Using Activated Taro Residue Carbon as an Adsorbent"** and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirements for the Master of Science in Chemistry **(Analytical).**

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Declaration

I the undersigned declare that this **“Removal of Hexavalent Chromium from Aqueous Solution Using Activated Taro Residue Carbon as an Adsorbent”** is my original work and has not been presented for any degree in any university and all the resource of materials used for this Thesis have been duly acknowledged.

Name of Student Signature Date

This MSc. Thesis has been submitted with our approval as advisors

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LIST OF ACRONYMS

ATRC	Activated Taro Residue Carbon
DPC	Diphenyl carbazide
FTIR	Fourier Transform Infrared Spectrophotometer
pHzpc	Point of zero charge
rpm	Rotation per Minutes
UV-Vis	Ultra violate visible spectrophotometer
XRD	X-ray Diffraction
PSO	Pseudo Second Order
PFO	Pseudo First Order

ABSTRACT

Hexavalent chromium, Cr (VI) is one of the major heavy metals of great concern in aqueous solution. Its removal from aqueous solution is crucial for environmental protection. In this study, the adsorption of Cr (VI) from an aqueous solution by preparing Activated Taro Residue Carbon (ATRC) was investigated. ATRC was characterized in terms of moisture content, ash content, volatile matter, x-ray diffraction, and FTIR. Batch adsorption experiments were used to study the efficiency of the adsorbent for the removal of Cr (VI). Different parameters as batch studies with different contact times, pH, adsorbent dose, and initial metal ion concentration were studied and the optimal conditions were established. The established optimal conditions include 180 min contact time, 5 g/L adsorbent dose, 5 mg/L initial metal concentration and pH 2. The percentage removal of Cr(VI) increased with increasing adsorbent dose from 1 to 10 g/L and contact time from 10 to 420 min and also decreased when the initial metal concentration increased from 1 to 50 mg/L. Freundlich isotherm model showed a better fit to the equilibrium data than the Langmuir model. The kinetics of adsorption for Cr(VI) was well represented by the pseudo-second order kinetic model. In the batch experiment the adsorption capacity Cr(VI) from aqueous solution using activated taro residue carbon as an adsorbent was around 8.93 mg/g and also the desorption studies of the adsorbent was examined. ATRC can be employed as an effective adsorbent and substitute for commercially available activated carbon for the removal of Cr(VI) from an aqueous solutions.

Keywords: *Hexavalent chromium, Batch adsorption, aqueous solution, X-ray diffraction, Fourier Transform Infrared, Activated taro residue carbon*

1. INTRODUCTION

Hexavalent chromium (VI) is a notorious environmental pollutant [1]. It's one of the most toxic heavy metals released by various industries such as tanning and leather industries, manufacturing industries, catalyst and pigments, fungicides, ceramics, crafts, glass, photography, electroplating industry and corrosion control application [2]. In aqueous media, chromium exists either as Cr (VI) or as trivalent, Cr (III). The toxicity of chromium depends upon its oxidation state, and thus Cr (VI) is highly toxic than Cr (III). In a solution, Cr (VI) exists in various forms such as chromate (CrO_4^{2-}), hydro chromate ($HCrO_4$), or dichromate ($Cr_2O_7^{2-}$) depending upon the pH of the solution [3]. Cr (VI) is a powerful oxidant and many of its compounds are highly soluble in water, and thus it is easily bioavailable [4].

A wide range of technologies, such as chemical precipitation, ion-exchange, membrane separation, reverse osmosis, electrodialysis, electrocoagulation, electrochemical treatment and adsorption, have been used to remove Cr (VI) from aqueous solution [5-8]. Membrane separation and electrochemical treatment are quite expensive, as they use much energy; Chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge and also huge sludge production, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [9]. Membranes replacement and the corrosion process are the problem of using electrodialysis. Ion exchange is considered as an alternative; however, it too is expensive and is characterized by poor selectivity for Cr (VI) ions [10]. In addition, adsorption has also taken the attention of scholars as the best alternative for the removal of Cr (VI) from an aqueous solution [11].

Adsorption is one in which certain adsorptive are selectively transferred from the fluid phase to the surface of particles suspended in an aqueous solution. It is a physical or chemical association of material molecules in the active sites of a surface through the weak Vander Waals or by forming chemical bonds with effective sites on the surface [12]. The adsorption method is cheap, has high efficiency for removal of metal from dilute solutions, release minimum chemicals, and biological sludge [13]. Removal of Cr (VI) from aqueous solutions by adsorption methods has been accomplished by exploiting its physical (physisorption), chemical (chemisorption) and biological (bioremediation) properties due to its dissolution tendencies in aqueous solutions [14].

Various adsorbents such as including synthetic polymers, activated carbons, biomass, graphene oxide, nanoparticles, and biosorbents have been investigated the for removal of Cr (VI) form aqueous solution [15-18].

Activated carbon derived from various agricultural byproducts such as sawdust activated carbon, almond shell activated carbon, activated tamarind seed, rice straw-derived carbon, bamboo charcoal, and corn stalk have been investigated for the removal of Cr(VI) from water [19-24]. However, most of these carbonizations were conducted at high temperatures which elevated the cost of production of activated carbon. The low temperature chemical carbonization has the potential to further reduce the cost of producing activated carbon from agricultural byproducts.

Taro (*Colocasia esculenta) Schott*) is an herbaceous, monocotyledonous, perennial stem root crop that is widely cultivated in tropical and subtropical regions of the world. It is originated from tropical areas of South and Southeast Asia and the Pacific Islands and then arrived on the east coast of Africa over 2000 years ago. Taro tubers are important sources of carbohydrates as an energy source and are used as staple foods in tropical and subtropical countries. It is largely produced for its underground corms which contains 70–80% starch [25].

The use of activated carbon produced from agricultural byproducts for removal of toxic environmental pollutants such as Cr (VI) is cost-effective. Therefore, a chemical activation method was employed in this study for the generation of activated Taro residue as an adsorbent for removal of Cr (VI) from an aqueous solution.

1.1. Statement of the Problem

These days, Environmental pollution is one of the most challenging problems that humans are facing. The discharge of industrial, agricultural, and domestic wastewaters without treatment or with inadequate treatment levels causes degradation of ecosystems. The inorganic pollutants such as include lead, mercury, cadmium, arsenic~~,~~ and Cr (VI) are hazardous to humans [26]. Hexavalent Chromium is one of the most harmful heavy metals [27], which is classified in the top priority list of toxic pollutants defined by the US Environmental Protection Agency (USEPA). Hexavalent Chromium can be released to the environment form several industries such as tanning, painting, dyeing, explosives, ceramics and wood processing as well as in the paper industry [28]. Cr (VI) is non-biodegradable and tends to bio-accumulate in living organisms causing serious disease and disorders [29]. In developing countries, like Ethiopia, where there is loose/weak environmental control, various industries release toxic chemicals like Cr (VI) into their surrounding environment. Various physical and chemical processes can be used for removal of metals from aqueous solution [30]. Some of this method includes chemical precipitation, ion-exchange, membrane separation, reverse osmosis, electrolysis, electrocoagulation, solvent extraction, electrochemical treatment and adsorption [5-8].

The major limitations of the existing Cr (VI) removal methods are sludge production, high operational cost and some of them are complex for the management. Therefore, it is imperative to search for alternative methods from easily accessible and cheap agricultural byproducts. Activated carbons obtained from agricultural byproduct have been shown promising removal efficiency for the removal of metal ions from aqueous solution. Therefore, in this study, chemically activated Taro residue was used as a new low-cost adsorbent to remove Cr(VI) from an aqueous solution. This residue has no use and is available at low prices. Thus, converting this byproduct to a useful product has dual advantages: reduce the cost of waste disposal and provide an alternative adsorbent to the existing commercial activated carbon for the removal of Cr (VI) from an aqueous solution.

1.2.Objective of the study

1.2.1. General Objective

The main objective of this study is to investigate the efficiency of activated carbon from taro residue for the removal of Cr(VI) from an aqueous solution.

1.2.2. Specific Objective

- To prepare activated carbon from Taro (*Colocasia esculenta (L.)* residue via chemical activation method using H_2SO_4
- To characterize synthesized adsorbent by using FTIR, XRD and other available techniques.
- To evaluate the adsorptive capacity of the synthesized activated carbon from Taro residue
- To optimize the adsorption parameters such as solution pH, initial Cr(VI) concentration, contact time, and adsorbent dose on the removal of Cr(VI) by synthesizing activated carbon from Taro residue
- To study adsorption isotherm and kinetics models that represents the adsorption of the Cr (VI) process.

1.3.Significance of the Study

This study has the following significances:

- It produces environmentally safe and low-cost activated carbon from agricultural byproducts (taro residue) for the removal of Cr(VI) from aqueous solution.
- It is significant in converting agricultural byproducts to an adsorbent that can be used for the removal of Cr(VI) or other metal ions.
- The finding of the study will be used as a reference for other researchers

2. LITERATURE REVIEW

2.1. Overview of Chromium

Chromium (Cr) is the 17th most abundant element in the earth's mantle [31]. It occurs naturally as chromite ($FeCr_2O_4$) in ultramafic and serpentine rocks or complexed with other metals like crocoite (PbCrO4), bentorite (Ca_6 (Cr, $Al)_2$ $(SO_4)_3$), and tarapacaite (K_2CrO_4) and vauquelinite ($CuPb_2CrO_4PO_4OH$) [32]. Cr is used in many industrial processes such as plating, alloying, and tanning of animal hides, water corrosion inhibition, textile dyes, and mordents, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber [33]. Chromium is a steel-gray, lustrous, hard metal. Like other transition metals, chromium has variable oxidation states. The most common oxidation states of chromium are 0, +2, +3, and +6, with +3 being the most stable. But only three oxidation states are found in nature; these are: Cr (0) which occurs in metallic form, whereas, Cr (III) and Cr (VI) as soluble CrO_4^{2-} and $Cr_2O_7^{2-}$compounds.

Both Cr (III) and Cr (IV) may exist in a different form in wastewater depending on various conditions. Inorganic Cr (III) may exist in aqueous solution as hydroxo species, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3^{-}$, $Cr(OH)_4^{-,}$ $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and a mixed ligand complexes, such as $Cr(OH)Cl^{+}$, $Cr(SO_4)^{+}$. However, Cr $(OH)^{2+}$ predominate at pH 5 [34]. Whereas Cr (VI) may be present in aqueous solutions mainly as chromate ($CrO_4^{\ 2-}$), dichromate ($Cr_2O_7^{\ 2-}$), hydrogen chromate ($HCrHO_4^{-}$), chromic acid (H_2CrO_4), and hydrogen dichromate ($Cr_2HO_7^{-}$), the last two species such as chromic acid (H_2CrO_4) and hydrogen dichromate ($Cr_2HO_7^{-}$) have been detected only in strongly acidic solutions. In typical surface waters when the concentration of Cr (VI) is >5 μg/L only $HCrO_4^{-}$ and CrO_4^{2-} can be found [34].

2.2.Toxicity of Chromium

In the aqueous environment, Cr(III) may hydrolyze into several species including $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, neutral species $Cr(OH)_3^{-}$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$ [35]. These hydroxides are less mobile, soluble, and toxic to living organisms due to their tendency to form complexes with organic ligands (natural organic matter) in the environment [36]. Cr (VI) hydrolyzes to $Cr_2O_7^{2-}$, CrO4^{2-} and $HCrO_4^{-}$ which are strong oxidants [37]. The Cr (VI) compounds are more mobile and soluble, making them bioavailable. These compounds are toxic as they are associated with a variety of detrimental health effects such as skin rash, weakened immune system, nose irritations, and nose bleed, ulcers, allergic reactions, kidney and liver damage, genetic material alteration, gastric damage, and even deaths [38]. The toxicity of Cr (VI) on humans has been primarily associated with the chemical structural resemblance between Cr oxyanions [CrO_4^{2-}] and sulphate ions [SO_4^{2-}] making the former able to cross the biological membranes using sulphate routes [39].

2.3.Chromium Removal Method

Several treatment techniques have been used for the removal of Cr (VI) from an aqueous solution. These include techniques such as membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis, ion exchange (IE), Chemical precipitation, adsorption, and photoreduction [40].

2.3.1. Membrane Separation

A membrane is a barrier that separates two phases from each other by restricting the movement of components through it in a selective style. Membranes have been used since the 18th century for wastewater treatment. Since then, a lot of improvements have been taken place to make membranes better suited for many different applications [41]. It can also 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. Different membrane-based technologies including reverse osmosis (RO), nanofltration (NF), ultrafiltration (UF), microfiltration (MF), and electrodialysis (ED) have been used for wastewater treatment. It has been used in place of traditional treatment processes like physical separation techniques, chemical treatment, biological treatment, etc. Different types of membranes have been used for the removal of Cr (VI) from wastewater. UF uses a permeable membrane to separate heavy metals, macromolecules, and suspended solids from inorganic solution based on pore size (5–20 nm) and molecular weight of the separating compounds [42]. RO, UF, and MF are conceptually similar processes, but they differ in terms of the pore diameter (or apparent pore diameter) of the membrane used [43, 44]. Table 1. shows different membranes which have been employed for removal of Cr (VI) from aqueous solution.

Table 1 Membranes which have been used to remove Cr(VI)

Membrane	**Initial Cr (VI) Conc. mg/L**	**Removal system**	**Wastewater**	**Rejection rate %**
Carbon membrane	1000	Batch	Synthetic	96
Nitrated carbon membrane	1000	Batch	Synthetic	84
Aminated carbon membrane	1000	Batch	Synthetic	88
Polymer-enhanced ultrafiltration	10	Continuous	Synthetic	30
Composite polyamide membranes	1000	Continuous	Synthetic	99
Composite polyamide membranes	1000	Continuous	Synthetic	94
Polyacrylonitrile fiber	0.2	Continuous	Synthetic	90

ED is an electrochemical process for the separation of ions across charged membranes from one solution to another [45]. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents, and salt production**.** Recently, Raghava Rao and coworkers used ED to recover chromium salts and other neutral salts residual for tanning baths. In their study, the percentage of extraction observed was around 90 % for chloride and 50 % for sulfates. Their finding has opened new possibilities for the reuse of water, neutral salts, and chrome, without any problems in process control or effluent treatment. ED is an electro-driven membrane process involving ion-exchange membranes [46]. Compared to other kinds of membrane technologies, ED uses electrical current, rather than pressure, to induce the ions to pass through the membrane. The use of pressure is a major cost factor for other membrane processes. The cost of ED can be reduced by using low levels of electrical current [47].

Reverse Osmosis

The RO process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity [48]. RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. Dialynas and Diamadopoulos [49] applied a pilot-scale membrane bioreactor system in combination with RO and found heavy metal removal efficiencies were very high. The major drawback of RO is the high power consumption due to the pumping pressures, and restoration of the membranes.

2.3.2. Ion - Exchange

IE processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency, and fast kinetics [50]. IE resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in IE processes, synthetic resins are commonly preferred as they are effective for the removal of heavy metals from the solution [51].

The common cation exchangers are strongly acidic resins with sulfonic acid groups (-SO_3H) and weakly acid resins with carboxylic acid groups (-COOH) [52]. Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. Cation exchangers are effective for removal of Cr (III), while anion exchangers are appropriate for Cr (VI) removal [53]. For removal of Cr (VI), strong-basic anion exchangers, with an exchangeable counter ion of Cl_2, are commonly used [54].

Theoretically, anion exchange with synthetic resins is considered an ideal process for chromium removal because chromate is the most common anions present in water. Because of the positive charge of Cr(III) and the negative charge of Cr(VI), a two-step ion exchange process, which use of a cation resin for Cr(III) removal followed by use of an anion resin for Cr(VI) removal could be effective if both species were present [53].

2.3.3. Chemical Precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate [55]. Precipitation is a method of causing contaminants that are either dissolved or suspended in solution to settle out of the solution as a solid precipitate. The precipitate can then be filtered, centrifuged, or otherwise separated from the liquid portion. A coagulant is a precipitating agent that causes the smaller particles suspended in solution to increase their particle size for settling down as sludge [35].

The most widely used chemical precipitation technique is hydroxide precipitation, due to its relative simplicity, low cost, and ease of pH control [56]. Hydroxide precipitation process using $Ca(OH)_2$ and NaOH in removing Cu(II) and Cr(VI) ions from wastewater was evaluated. In the procedure, Cr (VI) has been converted to Cr (III) using ferrous sulfate. The maximum precipitation of Cr (III) was observed at pH 8.7 with the addition of $Ca(OH)_2$ and the concentration of chromate was reduced from 30 mg/L to 0.01 mg/L [57]. The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control [58]. Common precipitant and their characteristics are presented in Table 2. Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that the solubility of the metal sulfide precipitates is dramatically lowers than hydroxide precipitates and sulfide precipitates are not amphoteric [54].

Table 2 Common precipitants and their characteristics

Chemicals	Characteristics
Alum	Alum is an off-white crystal which, is dissolved in water, produce acidic solution
Ferric chloride	Ferric chloride ($FeCl_3$) is available in either dry or liquid form.
Lime	Lime is available in many forms, with quicklime (CaO) and hydrated lime [Ca(OH)2] being the most common forms
Polymer	Polymers may be available as a prepared stock solution ready for addition to the treatment process or as a dry powder

2.3.4. Electrochemical Method

The electrochemical method involves the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and expensive electricity supply, so they haven’t been widely applied. However, with the stringent environmental regulations regarding wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades [52]. Electrochemical methods involve such as electrocoagulation, electro flotation (EF), and so on.

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes [59]. The metal ions generation takes place at the anode; hydrogen gas is released at the cathode. The hydrogen gas would also help to float the flocculated particles out of the water [60]. In an electrocoagulation process, no addition of chemicals is necessarily needed. A small volume of sludge is produced, compared with that in classical chemical process, which can be easily removed by decantation. In the case of the treatment of wastewater containing Cr (VI), the application of this technology implies a preliminarily reduction step, i.e., converting Cr (VI) to Cr (III) [61].

EF separates pollutants by floating them to the surface of the liquid phase [62]. EF has wide range of applications in heavy metals removal from industrial wastewater. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. The method was first proposed by Elmore in 1904 for the flotation of valuable minerals from ores [44].

2.3.5. Adsorption

Adsorption is considered a phase transfer process that is generally used to eliminate chemical pollutants from various wastewaters and gases [44]. Adsorption is a surface phenomenon and is defined as the increase in the concentration of a particular component at the surface or interface between two phases [63]. There are mainly three distinct mechanisms for adsorption. These are steric, equilibrium, and kinetic mechanisms. Steric separation allows the molecules to enter having less pore diameter of the porous solid and excludes the larger molecules. In the equilibrium mechanism, molecules having stronger adsorbing power are preferentially separated by the adsorbent. The kinetic mechanism is based on the different rates of diffusion of various molecules into the pore of the solid; thus, by controlling the time of exposure fast diffusing molecules are preferentially separated by the adsorbent [64]. Adsorption is mostly an exothermic process due to the decrease in surface energy of the adsorbent impelled by the inhibition of the adsorption site atoms' movement induced by the attachment of adsorbate molecules [63]. Adsorbates may attach to the adsorbent through electrostatic attraction, ion exchange, ion pair interactions, van der Waals forces, and hydrophobic hydration [65].

2.3.5.1. Types of Adsorption

2.3.5.1.1. Physical Adsorption

Physical adsorption is generally occurs in any solid/liquid or solid/gas system [66]. Physical adsorption is a process in which the binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction, hydrogen bond, and dipole interaction. Physisorption is non-specific in nature and is generally regarded as a weak, reversible process governed by competitive adsorption and desorption which takes place at different rates at the heterogeneous surface [67]. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. Commercial adsorbents utilize physical adsorption for their surface binding.

2.3.5.1.2. Chemical Adsorption

It is a kind of adsorption that involves a chemical reaction between the adsorbent and the adsorbate [66]. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (covalent or ionic). Chemisorption is irreversible and very specific in nature, and depends primarily on the proportionality of the surface area [68] In general, the main steps involved in the adsorption of pollutants on solid adsorbent are:

- Transport of the pollutant from the bulk solution to the external surface of the adsorbent.
- Internal mass transfer by pore diffusion from the outer surface of adsorbent to the inner surface of porous structure and
- Adsorption of adsorbate on the active sites of the pores of adsorbent.

The overall rate of adsorption is decided by either film formation or intraparticle diffusion or both as the last step of adsorption is rapid as compared to the remaining two steps.

2.3.5.2.Adsorbent

Different types of natural and commercial adsorbents have been used for the removal of Cr (VI) from aqueous solutions. Some of these adsorbents are described in the subsequent section

2.3.5.2.1. Natural Adsorbent

Rice Husk

Yogeshwaran and coworkers [69] investigated the removal efficiency of adsorbent prepared from Rice husk (RH) for Cr (VI) from the aqueous solutions. They observed that the maximum adsorption capacity of RH adsorbent was 80% at the pH of 3. However, when the pH was raised to 5m its adsorption capacity was decreased to 68%. . The adsorption was also fitted Langmuir isotherm and the maximum concentration of Cr (VI) was removed at 150 min.

Banana Peels

Banana peels were used as an adsorbent to remove the Cr (VI) from the aqueous solution. The process of adsorption was carried out using potassium dichromate ($K_2Cr_2O_7$) solution [70]. The maximum adsorption capacity of chromium using these GBPs was 96% at the optimum pH value of 3. The adsorption data is fully fitted for Langmuir and Freundlich Isotherm models

Mango kernel

Mango kernel powder is activated with Phosphoric Acid as an adsorbent to remove the chromium from the industrial effluent [71]. Then, he found that the maximum adsorption capacity of Chromium was 7.8 mg/g at the pH of 2 and the temperature of 35°C. Finally, he concluded that the Langmuir Adsorption Isotherm is represented the equilibrium data is good and the adsorption kinetics was represented in pseudo-second order relation

2.3.5.2.2. Commercial Adsorbent

Graphene

Graphene has a two-dimensional structure, high specific surface area (theoretically ~2600 m2/g), good chemical stability and other excellent properties [70]. It is available in various forms such as pristine graphene, graphene oxide and reduced graphene oxide. Graphene may be oxidized to add hydrophilic groups for heavy metal removal. Graphene oxide has been reported for removal of chromium, it exhibited maximum adsorption capacity which was 92.65 mg/g at an optimum pH of 5. This adsorption of chromium on graphene oxide was found to be endothermic and spontaneous [72].

Activated Carbon

Activated Carbon is an adsorbent derived from carbonaceous raw material, in which thermal or chemical means have been used to remove most of the volatile noncarbon constituents and a portion of original carbon content, yielding a structure with a high surface area. Production of active carbon began in 1900-1901 to replace bone char in the sugar refining industry and powdered activated carbon was first produced commercially in Europe in the early 19th century, using wood as a raw material [73]. Activated carbon can be obtained from any material which has high carbon content. Activated carbon is a good adsorbent for chromium removal because it has a well-developed porous structure and a high internal surface area for adsorption [67]. However, coal-based activated carbon is expensive, its use has been restricted and further efforts have been made to convert cheap and abundant agricultural waste into activated carbon [74].

2.3.5.3.Factors Affecting Adsorption Process

Many physicochemical factors can influence the adsorption efficiency of the adsorbate. These factors include: initial metal concentration, temperature, pH and contact time between adsorbate and adsorbent dosage. In addition, the presence of other anions and cations, metal speciation, pollutant solubility and form, etc. may also influence the efficiency of the method [75].

I. Effect of pH

pH is one of the most important environmental factor used to determine the adsorption of heavy metal ions; the value strongly influences the properties of both adsorbates and adsorbents such as the ionic state of functional groups present on the adsorbent as well as the chemical properties of the studied metal in solution [76]. The 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 decreases for cationic species adsorption, while for anionic species percentage removal increases [73]. Adsorption of Cr (VI) is highly influenced by the pH of the solution. The removal efficiency of Cr (VI) decreases with an increase in pH. According to Memon and coworkers [77] from aqueous solution mainly containing, $HCrO_4^{-}$, 73.8% Cr (VI), was removed at pH 2. In the case of chromate, the lower pH resulted in higher adsorption as the positively charged surface of the adsorbent [78].

II. Effect of contact time

Adsorption is also affected by contact time between the surface of the adsorbent and the solution containing metals (adsorbate). Adsorption proceeds fast and most adsorption takes place at the very beginning of the process [79]. In adsorption systems, contact time plays a vital role irrespective of other experimental parameters. The determination of the optimum contact time needed to achieve the highest removal efficiency for the metal ions is very important in batch adsorption experiments. According to Lubanga et al. [80] observed Cr (VI) rapid rate of adsorption leading up to 85.91% Cr (VI) removal during the first 10 min by Artocarpus heterophyllus Seed Powder adsorbent and then, a gradual rise of adsorption rate up to 98.73% in 90 min

III. Initial metal Concentration

The initial concentration of the adsorbate is important in adsorption, since a given mass of sorbent material can only adsorb a fixed amount of adsorbate. Normally, the adsorbate removal efficiency decrease with an increase in its initial concentration. The higher the concentration of the adsorbate, the smaller the amount it can remove. When the initial concentration increases, the active sites of the adsorbent surface can be occupied and thus adsorption sites are lacking to adsorb more adsorbate. However, the actual amount of adsorbate adsorbed per unit mass of adsorbent increased with an increase in concentration. This may be due to the high driving force for mass transfer at a high initial concentration [73]. Garg et al., [81] observed that the absorption efficiency of sugarcane bagasse and maize corn cob adsorbents increased up to 5.75 mg/g and 3.0 mg/g, respectively. Then, at higher concentrations, their adsorption efficiency became constant, indicating the saturation of the active sites of the adsorbent.

IV. Adsorbent Dosage

The concentration of both the adsorbate and the sorbent is a significant factor to be considered for an effective adsorption process. The adsorbent dosage is an important parameter to determine the capacity of an adsorbent. The effect of adsorbent dosage on adsorption is studied by varying the amount of adsorbents and keeping the other parameters constant. For instance, Parlayici and Pehlivan [82] investigated adsorbent doses of banana peels for removal of Cr (VI) and observed 34.55% at 2.5 g/L and 94.15% at 25 g/L. The uptake capacity of adsorbent raises with an increase in adsorbent, this appears due to the increase in the available binding sites of the adsorbent.

V. Particle size of adsorbent

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, the particle size of a material is a very important component in understanding how your product performs [83]. Smaller particle sizes reduce internal diffusion and mass transfer limitation to penetrate of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained) [84].

2.4. Adsorption Process Modeling

Assessment of a solid–liquid sorption system is usually based on two types of investigations: equilibrium batch sorption tests and dynamic continuous-flow sorption studies. Equilibrium isotherm model equations such as Langmuir and Freundlich are used to describe experimental adsorption data in batch mode. It is important to find the best-fit isotherm to evaluate the efficiency of the prepared adsorbent to develop suitable industrial adsorption system designs [85].

2.4.1. Adsorption Isotherms

An adsorption isotherm models are used to describe the phenomenon governing the retention (or release) or agility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [86].

2.4.1.1. Langmuir Adsorption Isotherm

Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents [87]. Langmuir adsorption isotherm is widely used to describe the relationship between the amounts of adsorbate adsorbed onto the adsorbent, its equilibrium concentration in aqueous solution. It uses the following three assumptions: (i) the surface of the adsorbent is in contact with a solution containing an adsorbate which is strongly attracted to the surface; (ii) the surface has a specific number of sites where the solute molecules can be adsorbed; (iii) the adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption. The Langmuir equation is

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad 1$$

Where qe is the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g dry weight), q_{max} is the maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface-bound at high C_e, C_e is concentration of metal ions in solution at equilibrium and K_L is a Langmuir constant. The linear form is

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} C_e \qquad 2$$

The value of q_{max} and b computed from slope and intercept of the Langmuir plot of Ce/qe versus Ce. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant [separation factor] [88].

$$R_L = \frac{1}{K_L C_o} \qquad 3$$

Where Co initial concentration R_L value indicates the adsorption nature to be either unfavorable if $R_L>1$, linear if $R_L=1$, favorable if $0<R_L<1$ and irreversible if $R_L = 0$.

2.4.1.2. Freundlich Adsorption Isotherm

The Freundlich isotherm is the oldest known two-parameter adsorption model which is applied for multilayer, heterogeneous adsorption sites [89]. Freundlich isotherm describes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. The empirical Freundlich model also considers monomolecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption

$$q_e = K_F Ce^{1/n} \qquad 4$$

Where Ce = the equilibrium concentration of adsorbate (mg/L), qe = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), K_f and 1/n are Freundlich constants. K_f and n are indicators of adsorption capacity and adsorption intensity respectively. The linear form is

$$\log q_e = logK_F + \frac{1}{n}logC_e \qquad 5$$

If n =1 then the partition between the two phases are independent of the concentration. If the value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption.

2.5.Analytical Instrument

2.5.1. Fourier Transform Infrared

Infrared spectroscopy probes the molecular vibrations [90]. The IR region is lying between visible and microwave end of the electromagnetic radiation spectrum. It is basically divided into three main portions: near IR (14000– 4000 cm^{-1}), mid-IR (4000–400 cm^{-1}), and far IR (400–40 cm^{-1}). IR measured the amount of radiations absorbed by the molecule and their intensity. Fourier transform infrared spectroscopy (FTIR) is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiations [91].

2.5.2. X-ray diffraction

X-ray diffraction was used to determine crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample [92]. X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s law:

$$n\lambda = 2d\sin\theta \qquad 6$$

Where n is an integer, λ is the wavelength of the X-rays, d is the interpalanar spacing generating the diffraction, and u is the diffraction angle.

3. METHOD AND MATERIAL

3.1.Chemicals and Instruments

3.1.1. Chemicals

The chemicals used for the study were: potassium dichromate, $K_2C_{r2}O_7$ (99.5%, FINKEM, England),), Acetone from (99.9%, BDH Chemicals Ltd) 1,5 diphenyl carbazide (DPC), (98%, Analar, England), Sulphuric acid, H_2SO_4 (98%, UNI CHEM, Germany), Hydrochloric acid, HCl (37%, Riedel-deHaën, Germany), Sodium hydroxide, NaOH (90%, BDH, England). All chemicals were analytical reagent grade and used without further purification.

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 (AFE-110L), thermostatic water bath (Model, GrantGLS400, England) was used for mixing of the adsorbent in the solution, and oven (model GENLAB WLDNES, England) was used for drying purpose. FTIR spectrophotometer (Spectrum 65FT-IR,Perkin Elmer, USA)) and X-ray diffraction (XRD), model 7000, (Shimazu, Japan).

3.2.Preparation of Stock Solution

The stock solution of Cr (VI) having a concentration 1000 mg/L was prepared by dissolving 2.8287 g dried crystalline of $K_2Cr_2O_7$ in 1000 mL of distilled water. A working solution, 100 mg/L of Cr (VI) was prepared by dilution. A series of standard solutions were prepared from the working solution by further dilution for the construction of calibration curve. 0.01 M NaCl, 0.1 M HCl, and 0.1 M NaOH were also prepared and used when required

3.3.Preparation of the Adsorbent

Raw Taro residue was collected from Tepi, south west region, Ethiopia. The residue was collected in polyethylene bags and transported to Jimma University Analytical Chemistry Post Graduate Research Laboratory. Then, it was washed with distilled water to remove dust and other impurities and kept in a drying oven at 105 ^oC for 24 hours. The dried Taro residue was treated with 98% H_2SO_4, in a ratio of 1:1 (Taro residue: H_2SO_4, w/v), and again placed in an oven at 100 °C for 24 h to carbonize the raw adsorbent. After carbonization, the materials were mixed with deionized water and agitated to remove the unreacted acid [93]**.** The mixture was filtered through Whatman filter paper Cat No 1540-110 (110 mm. The material was washed repeatedly by soaking in 1% $NaHCO_3$ solution to remove the remaining acid. Finally, the prepared carbonized adsorbent or activated taro residue carbon (ATRC) was dried in an oven at 100 °C and ground, and stored in a desiccator until it was used.

3.4.Characterization of Adsorbent

3.4.1. Determination of Moisture Content

1.79 g of ATRC was taken in the pre-weighted crucible and placed in an oven at 105 °C until a constant mass was obtained. The loss in weight of the ATRC shows the percentage of the moisture content [94].

$$\text{Moisture content}(\%) = \frac{W_1 - W_2(\text{g})}{\text{Wt. of sample}(\text{g})} * 100 \qquad 7$$

Where, W_1 = initial weight of crucible + sample, W_2 = final weight of crucible + sample

$$\text{Dry matter } (\%) = \frac{\text{Oven dry weight}(\text{g})}{\text{Initial Sample weight}(\text{g})} * 100 \qquad 8$$

3.4.2. Determination of Ash Content

From the dried ATRC, 1.5 g was taken in a porcelain crucible and placed in a muffle furnace at a temperature of 550 ^oC for 5 h [95]. Then, the resulting ATRC e was cooled in desiccators and weighed again. The heating, cooling and weighing cycle was repeated until a constant weight was obtained. Finally, the weight loss was recorded as the ash content of the adsorbent. The ash content was calculated as:

$$\text{Ash content} = \frac{(W_3 - W_1)(\text{g})}{(W_2 - W_1)(\text{g})} \times 100 \qquad 9$$

Where, W_1= weight of the crucible, W_2= weight of the crucible and sample before igniting, W_3= weight of crucible and sample after igniting

3.4.3. Volatile Matter

To determine the volatile matter of the material, 1.53 g of sample was added to the crucible and weighed. The content was placed in the muffle furnace at a temperature of 650 °C for 10 minutes. Then, it was taken out and kept in the desiccators for 30 min to cool down [96]. Eventually, volatile matter content in the sample was calculated by using the formula

$$Volatile\ matter(\%) = \frac{(W_2 - W_1) - (W_3 - W_1)}{W_2 - W_1} \times 100 \qquad 10$$

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

3.4.4. Fixed Carbon Content

The fixed carbon of samples was calculated by subtracting the sum of moisture content, ash content (%), and volatile matter (%) from 100 [97]

$$Fixed\ carbon\ content = 100 - (\%moisture + \%Ash + \%Volatile) \qquad 11$$

3.4.5. pH of Adsorbent

To measure the pH of the prepared adsorbent, 0.5 g of ATRC was dissolved in 30 mL in 50 mL plastic bottles. Then, and the content was shaken for 24 h in thermostatic water bath. The mixture was allowed to stabilize and the pH was measured [98].

3.4.6. Point of Zero Charge

The pH at the point of zero charges (pH_{PZC}) of the adsorbent was determined by the solid addition method [99]. Accordingly, 0.01 M NaCl was separately taken in 11 plastic bottles. Then, the solution in each bottle was adjusted to different pH values between ranging from 2 to 12, using 0.1 M HCl and 0.1 M NaOH. After adjusting the pH, 0.1 g adsorbent was added to each flask and the mixture was continuously stirred for 24 h at room temperature. Finally, the pH of the resulting solution was measured to determine pHzpc.

3.4.7. Fourier Transform Infra-Red Analysis

The Fourier transform infrared (FTIR) spectrometer is used to identify the functional groups present in the selected sample adsorbent in the wavenumber range of 400 - 4000 cm^{-1}. Firstly, the ATRC was mixed with potassium bromide (KBr) and the mixture was pressed as a pellet before analysis [100]. The sample was analyzed at the range of 400 - 4000 cm^{-1} before and after (Cr (VI)) adsorption for each using Fourier transform infrared spectrometer to see the functional groups that might involve in the sorption of chromium.

3.4.8. X- ray diffraction analysis

XRD analysis was performed on Cr(VI) loaded and unloaded ATRC to determine the degree of crystalline or amorphous nature of the ATRC. ATRC powder adsorbent was ground to fine particles and analyses were performed by varied diffraction angle (2θ) from 10 to 85 [101], analyzed by X-ray diffract meter (XRD) equipped with a Cu target for generating a Cu Kα radiation.

3.5.Batch Adsorption Studies

The batch adsorption of Cr (VI) was performed by mixing (5 g/L) of ATRC with 5.0 mg/L concentration Cr(VI) solution of in a 50-mL plastic bottle. The bottles were horizontally agitated in an incubated agitator at 200 rpm for 180 min at 25 °C. The solution was filtered using Whatman filter paper Cat No 1540-110 (110 mm). The concentration of Cr (VI) was monitered by UV-Vis spectrophotometry after complexing it with 1,5-diphenylcarbazide in acetone. The complexing procedure was done as follows. A 2 mL Cr (VI) was transferred to a glass test tube. Sulphuric acid (0.2 M, 1 mL) and 1,5-diphenylcarbazide (0.25% w/v, 1 mL) were added. Then, mixture was gently shaken and left for 5 min. Finally, the absorbance was measured at 544 nm against the reagent blank [102]. The amount of Cr (VI) removed (% removal) was calculated as:

$$(\%)\ \text{removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad 12$$

Then, the adsorption Cr (VI) capacity per unit mass of the adsorbent was calculated according to the following expression:

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad 13$$

Where C_i and Ce are the initial and final chromium concentrations (mg/L), respectively, qe is the amount of Cr (VI) adsorbed onto adsorbent (mg/g), V is the total volume of solution (L), and m is the adsorbent dosage (g).

3.5.1. Effect of pH

The effect of pH on the removal efficiency of sorbent for Cr (VI) metal ions was investigated from pH 1 to 7. To study the effect of pH, concentration 4 g/L of the prepared adsorbent was added to 50 mL polyethylene plastic bottle containing 5.0 mg/L Cr (VI). The pH of the solution was adjusted to different pH (1 - 7) using 0.1 M HCl and 0.1 M NaOH. The content was agitated at 200 rpm for 2 hrs. The absorbance of the filtrate was measured at 544 nm after complexing with 1,5-diphenylcarbazide.

3.5.2. Effect of Contact Time

The effect of contact time was studied by varying the contact time from 10 - 400 min keeping another parameter constant. Accordingly, this was done by weighing 4 g/L ATRC adsorbent was added to a solution containing 5 mg/ L of Cr (VI) ion. Subsequently, the content was shaken in a thermostatic water bath shaker at 200 rpm (25 °C) for 10 - 420 min. Then, the solution was filtrated through Whatman filter paper. Finally, the absorbance of the filtrate was measured at 544 nm after complexing with 1,5-diphenylcarbazide. The equilibrium time was determined at a time with the highest percent removal of Cr (VI).

3.5.3. Effect of Adsorbent Dose

The effect of changing the adsorbent dose on the adsorption rate of Cr(VI) was studied by adding the various amount of the adsorbent from 1 to 10 g/L to a solution containing 5 mg/ L of Cr(VI) ion. After adjusting other parameters conditions, and performing the required experiments, the resulting solution was filtered using Whatman filter paper. Finally, concentration of unabsorbed Cr (VI) was determined by spectrophotometry after complexing with 1.5-diphenylcarbazide.

3.5.4. Effect of Initial Cr(VI) Concentration

To determine the effect of Cr (VI) initial concentration, various concentrations ranging from 1 to 50 mg/L were investigated. Other parameters were kept constant, and the analysis was done following the procedure used in the former

3.6.Reusability Studies

To investigate, the reusability of the adsorbent, initially, 5 mg/L of Cr(VI) was absorbed using 5 g/L ATRC at pH 2. After the adsorption experiment, the adsorbents were collected by filtration and allowed to dry. Then, they were transferred separately into 25 mL 1.0 M of NaOH solution agitated for 180 min at 200 rpm and filtered. Above adsorption was repeated, and the metal ion concentration was measured at a time to evaluate the adsorption efficiency.

3.7.Adsorption isotherm Studies

Isotherm experiments were carried out in 50 mL plastic bottle kept at 25 ˚C in a horizontal shaker by varying the initial metal concentrations from 1 to 50 mg/L under optimal contact time (180 min) and optimum adsorbent dose (5 g/L). By measuring the concentrations at the initial time and at equilibrium, maximum adsorption capacity as well as removal efficiency were calculated. The results were found to be fitting both the Langmuir and Freundlich adsorption isotherm models expressed in equation 14 [103] and 16 [104] respectively.

$$q_e = \frac{(q_{max} b C_e)}{(1 + b C_e)} \qquad 14$$

Where Ce is the equilibrium concentration of the ion (mg/L); qe is the amount of ion adsorbed (mg/g); q_{max} is qe for a complete monolayer (mg/g); and b is the bio-sorption equilibrium constant (L/mg). The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor R_L, defined as:

$$R_L = \frac{1}{(1 + b C_0)} \qquad 15$$

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

Where q_e is the amount of ion adsorbed (mg/g); Ce is the equilibrium concentration (mg/L); K_F and 1/n are empirical constants, indicating the adsorption capacity (Freundlich constant) and adsorption intensity (which varies with the heterogeneity of the material), respectively.

3.8.Adsorption Kinetics Studies

The effects of time on the removal rate of Cr (VI) from the solution were investigated using kinetic study. Adsorption kinetics shows a large dependence on the physical and/or chemical characteristics of the adsorbent material [105]. The effect of time was studied at different time interval ranging from 15 - 420 min by maintaining another parameter constant. Finally, the obtained results were analyzed using non-linear pseudo first-order and pseudo-second order kinetics models in equation 17 and 18, respectively.

$$q_t = q_e(1 - \exp^{-k_1 t}) \qquad 17$$

$$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \qquad 18$$

Where 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.

Experimental data were assessed by intra-particle diffusion model to determine the rate controlling step and to find the adsorption mechanism. The presence or absence of intra-particle diffusion can be confirmed by applying the Morris Weber equation [106] as follows:

$$q_t = k_{tp} t^{0.5} + C_{in} t \qquad 19$$

Where qt (mg/g) is the amount of Cr (VI) adsorbed at time t, K_p (mg/g $min^{1/2}$) is the intraparticle diffusion rate constant and $C_{in}t$ is intercept that tells about thickness (mg/g) of the boundary layer.

4. RESULTS AND DISCUSSION

4.1.Screening of adsorbents

The removal capacity of different adsorbents has different capacities depending on the nature and characteristics of the adsorbent. In this work, different agricultural byproducts including *Teff* residue, Taro residue, jackfruit leave, jackfruit seed kernel, and jackfruit seed were examined for the removal Cr (VI) from aqueous solution. As can be seen from Figure 1 Taro residue, jackfruit seed and jackfruit leave exhibited removal efficiency for Cr(VI) from aqueous solution. Thus, Taro residue was selected in this study to investigate various parameters affecting its removal efficiency for Cr (VI) from an aqueous solution.

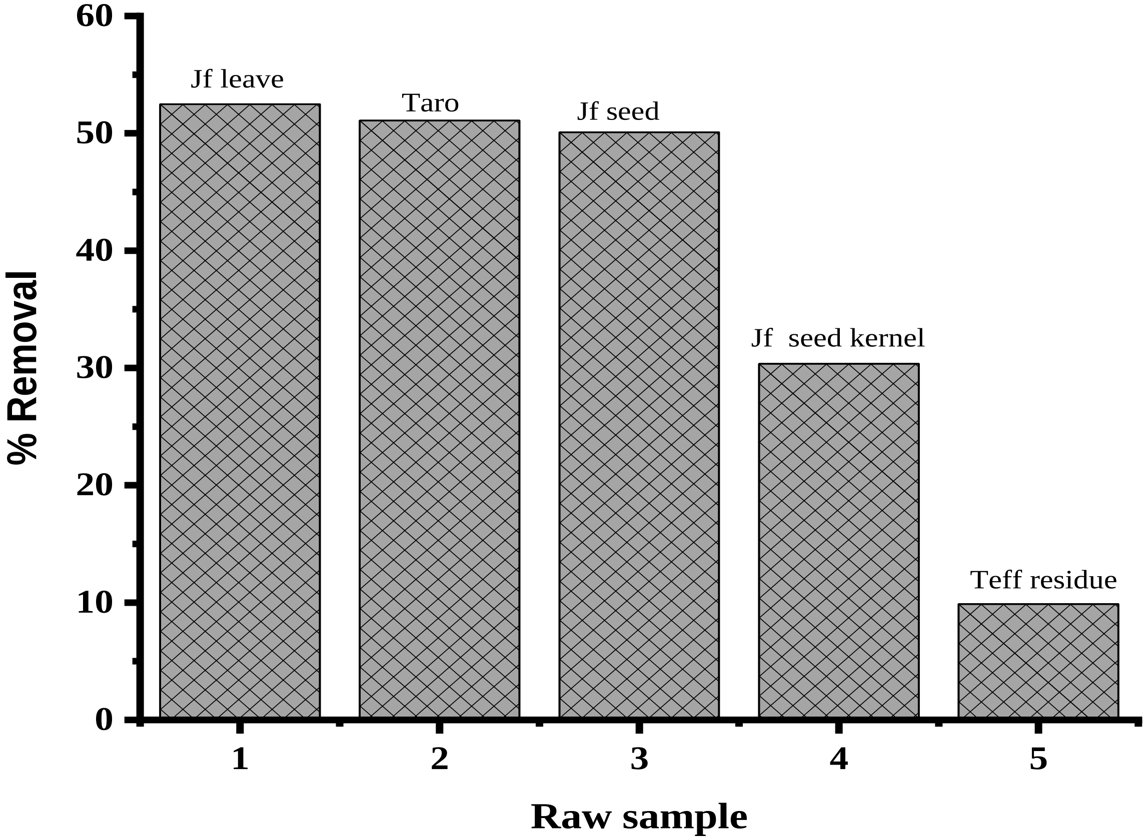

Figure 1: Screening of adsorbents: initial Cr(VI) concentration (5 mg/L), 4 g/L adsorbent dose, pH 2, contact time 2 hrs, shaking speed 200 rpm, at 25 °C

4.2.Characterization of Adsorbent

The moisture, dry matter, ash, volatile matter, fixed carbon and pH of the prepared adsorbent was investigated and the obtained results are presented in Table 3. -

Table 3: Physicochemical characteristics of activated Taro residue carbon

Parameter	Result
Moisture content (%)	7.2
Dry matter (%)	92.8
Ash (%)	10.8
Volatile matter (%)	57
Fixed Carbon	25
pH	6.60

The moisture content of a sample refers to the percentage of the water content of the sample. The **moisture and dry matter** contents of ATRC were 7.2%, and 92.8%, respectively. An adsorbent should contain low moisture content to have high adsorption efficiency. Because, water molecules can occupy high the adsorbent active site, and thus make adsorbed less efficient for removal of sorbate. [107]. Therefore, adsorption efficiency decreased with an increase in the moisture content of an adsorbent. The selected ATRC has lower moisture content than activated carbon produced from oil palm endocarp, reported earlier [108].

Ash is similar to the mineral matter content of a substance obtained after combustion [109]. It can influence the adsorptive capacity of the adsorbents as it is linked directly to the pore structure [110]. Ash value of ATRC was found to be 10.8%. The ash content of ATRC is lower than activated carbon produced from oil palm endocarp, reported earlier [108]. The ATRC has exhibited relatively higher volatile matter content, i.e., 57%.

4.2.1. Point of Zero Charge

The pHpzc of an adsorbent is a very important to determine the pH at which the adsorbent surface has a neutral electric charge. At this value the acidic or basic functional groups have no contributions to the pH of the solution [111]. Figure 2 shows a plot of the change of pH versus initial pH. The observed pHzpc of ATRC is 5.8. At pH values lower than pHzpc, the adsorbent surface is positively charged and therefore suitable for the sorption of Cr(VI). At pH values above pHzpc, the adsorbent surface is negatively charged and thus the adsorption of anions like Cr (VI) is lower at pH higher than pHzpc.

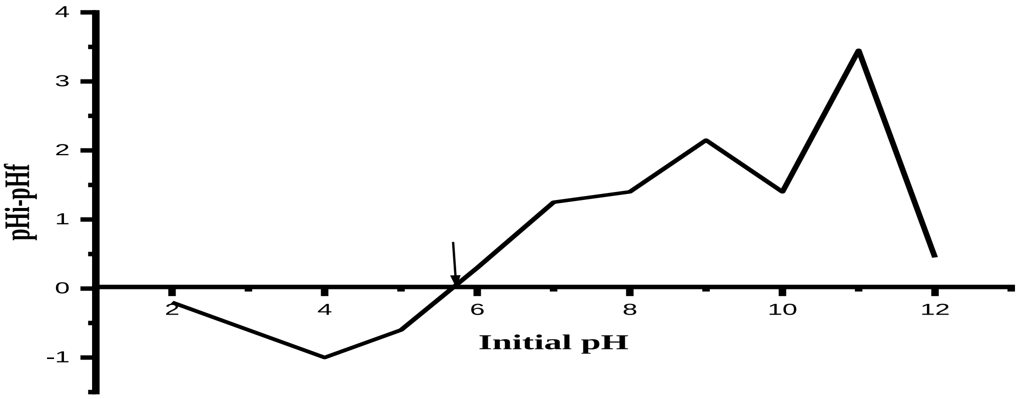

Figure 2: Determination of point of zero charges of **ATRC**

4.2.2. FTIR Analysis of Adsorbent

The FTIR spectra of ATRC (before and after sorption of CR (VI)) were used to determine the vibrational frequency changes in the functional groups of the adsorbent. The spectra of adsorbents were scanned from the 400–4000 cm^{-1} wavenumber range [112]. The FTIR spectra of ATRC before and after adsorption are shown in Figures 3a and 3b, respectively. The FT–IR spectra of ATRC before and after adsorption are shown in Figure 3a, the peak before adsorption give different peak around 3469 cm^{-1}, 2312 cm^{-1}, 1607 cm^{-1}, and 1360 cm^{-1}, the expected functional group of that peak are –OH (alcohol), C-H (alkane), C=C (Alkene) and C-O (carbonyl group) respectively and Figure 3b, show that the peak after adsorption gives different peak around 3453 cm^{-1}, 2825 cm^{-1}, 1612 cm^{-1} and 1364 cm^{-1} the expected functional group of this peak –OH (alcohol), C-H (alkane), C=C (Alkene) and C-O (carbonyl group), However in case of Cr(VI) loaded ATRC, there is a remarkable shift in positions and shapes of –OH and C=C peaks indicating Cr(VI) binding mostly with –OH and C=C groups.

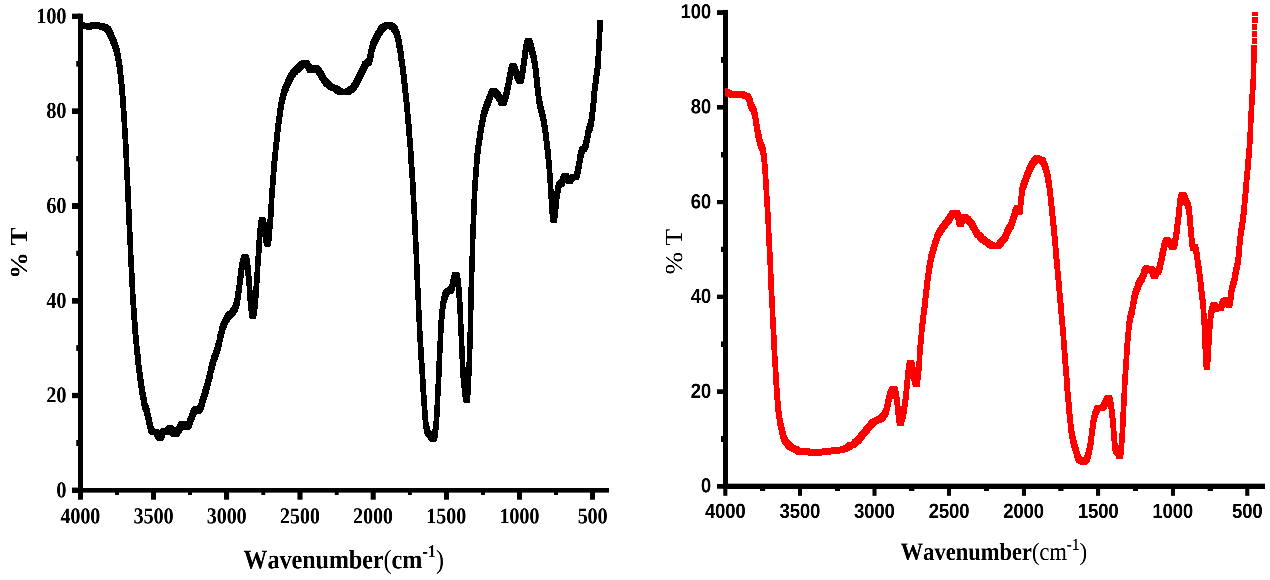

Figure 3: Fourier transforms infrared analysis of ATRC (a) before and (b) after adsorption

4.2.3. XRD Analysis of Adsorbent

XRD is used to determine particle size and whether the adsorbent is crystalline and amorphous [113]. The presence of broad peak and/or absence of a sharp peak in XRD spectra of a given adsorbent indicate that the adsorbent has an amorphous structure, which is an advantageous property for well-defined porous adsorbents [114]. XRD spectra of ATRC before loading and after loading of Cr (VI) are shown in Figure 4. The diffraction peaks for both Cr (VI) loaded and unloaded adsorbent were observed around the scattering angle (2θ) from 10 - 25^{o}. The diffracted pattern of the material shows broad peaks indicating that the prepared adsorbent is amorphous [115]. After loading Cr (VI), the XRD pattern of the adsorbent has exhibited a slight change, indicating the diffusion of Cr (VI) ions molecules in the micropore and macropore of the adsorbent [116]

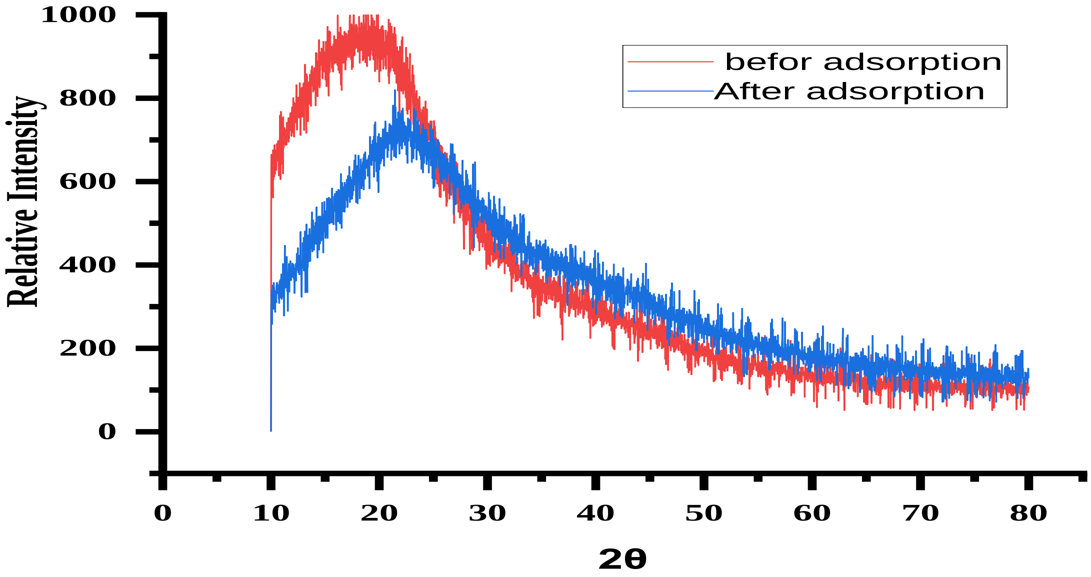

Figure 4: XRD spectra of ATRC before and after adsorption

4.3.Adsorption of Cr (VI)

4.3.1. Effect of pH

The pH of the aqueous solution is one of the important parameters that could affect the removal of heavy metals. Solubility and ionizability of the adsorbates, as well as concentrations of the counterion on the functional groups of the adsorbent, depends on the pH of a solution [117]. The effect of pH on removal of Cr (VI) was investigated by varying its values from 1- 7, while the other parameters were kept constant (Figure 5). It was observed that the maximum removal of Cr (VI), i.e., 97.5%, occurred at pH 2. However, when the pH was increased from 2 – 4, the amount of Cr (VI) removed by the adsorbent drastically decreased and then, kept almost constant at higher pH the removal efficiency of the ATRC for at lower pH, the surface of adsorbent would be surrounded by the hydronium ions (H^+), which could enhance the interaction of Cr (VI) with binding sites of the adsorbent.

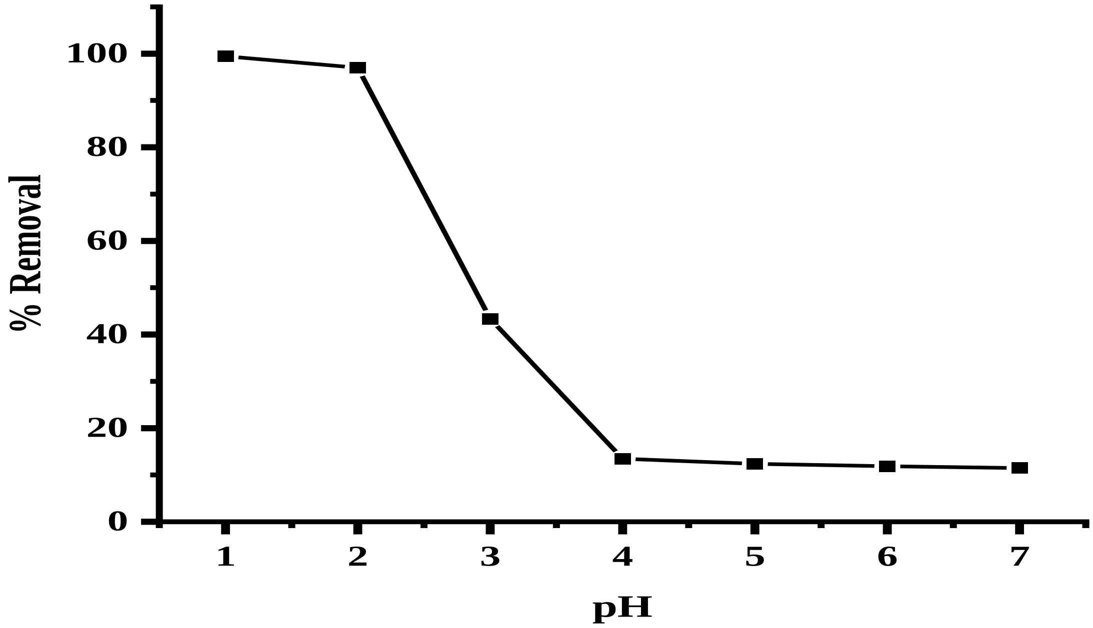

Figure 5: Effect of pH on removal efficiency: Contact Time 2 hrs, Dose 4g/L, initial Conc, 5 mg/L at 200rpm

In acidic pH, Cr (VI) predominantly exists as $HCrO_4^-$, whereas at higher pH CrO_4^{2-} or $Cr_2O_7^{2-}$ predominate. Therefore, the higher adsorption efficiency observed at lower pH is due to the strong electrostatic attraction between surface groups and $HCrO_4^-$ [118-120]. The interaction between $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ ion and adsorbent surface decreases at higher pH because the adsorbent surface becomes negatively charged, and also there is an abundance of OH^- in aqueous solution, which can be attributed to the competitive adsorption of $Cr_2O_7^{2-}$ and OH^- [118].

At low pH, a large quantity of hydronium ions (H^+) existed, which made the ATRC surface more positively charged, leading to a higher removal rate of Cr(VI) from the aqueous solution. Because, the binding of anionic Cr(VI) ion species is enhanced on the positively charged surfaces [121]. From the pHpzc study results, ATRC has a positive-surface charge at pH less than 5.8 and thus, only anionic species could be adsorbed onto the adsorbent below this pH

4.3.2. Effect of Contact Time

The effect of contact time was investigated by varying the contact time form 10-420 min. Figure 6 shows the results of the effect of contact time between adsorbent and adsorbate. It was observed that when the contact time increased from 10 to 60 min, the percent removal of Cr (VI) has shown slight increment, from 90.24 to 96.35% and then, exhibited constant removal efficiency above 120 min. The study results demonstrated that the adsorption process was fast in the first few minutes and then, a steep slope was observed after some minutes indicating the presence of physical adsorption, and eventually, the slope of absorption become very low indicating the resistance to mass transfer due to active sites saturation. When the available sites are occupied by metal ions, repulsive forces come into play between the bulk and the adsorbed molecules and reduce adsorption [122]. Once the available active sites are occupied with the target analyte, increasing the contact time does not increase adsorption, because after the equilibrium time after which adsorption capacity remains constant [123].

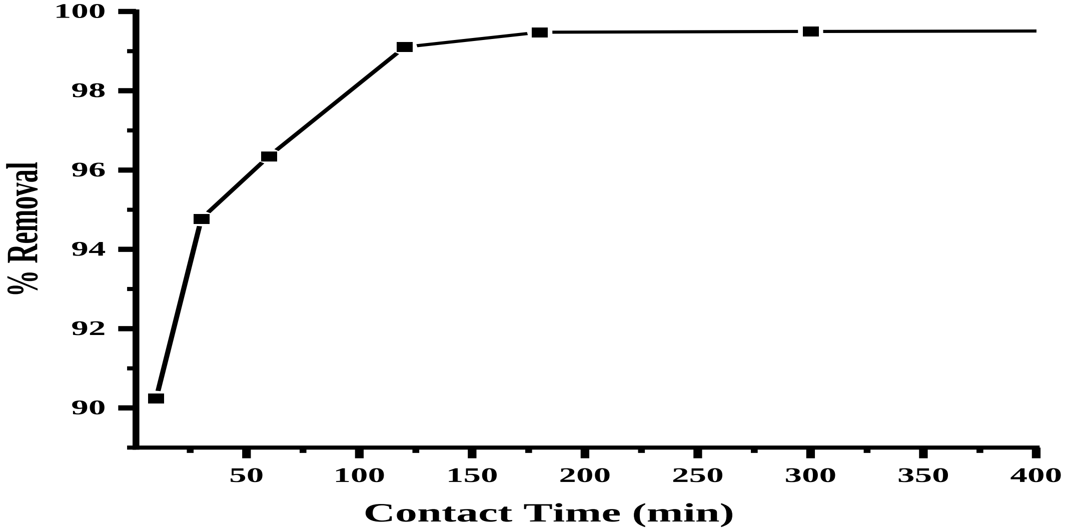

Figure 6: Effect of contact time on removal efficiency: pH 2, Dose 4 g/L, initial Conc 5 mg/L, rpm 200 and T 25^{o}C

4.3.3. Effect of Adsorbent Dose

The effect of the amount of adsorbent on the adsorption of Cr (VI) was studied and the results are shown in Figure 7. It was observed that the percent removal of Cr (VI) increases with increasing the amount of adsorbent added from 1 – 5 g/L and then, remain constant at higher doses. The removal efficiency of the adsorbent has increased as the dose of the adsorbent increases due to the availability of more binding sites [124]. However, after an optimum dose, the increase in the change in removal efficiency is minimal as the equilibrium state is attained between the adsorbate and adsorbent [125].

On the other hand, it was observed that the adsorption efficiency (qe) was decreased from 4.4 mg/g to 0.4 mg/g when the adsorbent dose was increased from 1 g/L to 10 g/L. Adsorption efficiency is inversely proportional to the mass of the adsorbent, and thus, when mass of the adsorbent increases the removal efficiency of the adsorbent decreases. The observed decrease in uptake of Cr with the increased adsorbent dose due to the unchanged initial concentration of metal ion and the substantial adsorption capacity of the smallest adsorbent dose or less availability of surface area per unit weight [126]. The reason for decreasing the removal efficiency may be an agglomeration of the adsorbent particles resulted in a decrease in total adsorbent surface area available to Cr(VI) ions or an increase in diffusion path length[127].

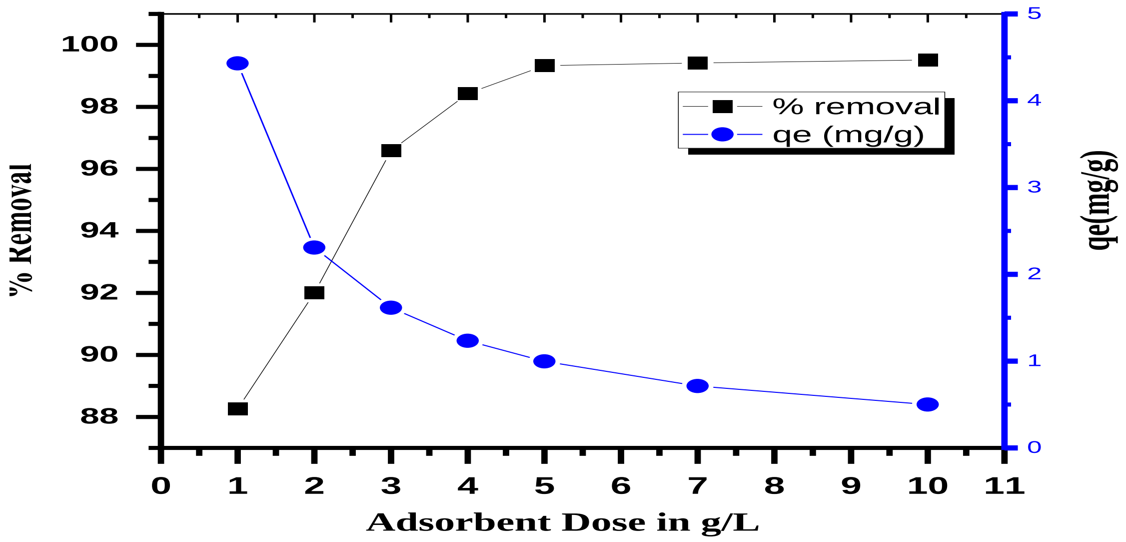

Figure 7: Effect of Adsorbent dose on removal efficiency and adsorption efficiency: pH 2, Contact Time 3hrs, initial Conc 5 mg/L, rpm 200 and T 25°C

4.3.4. Effect of Initial Cr (VI) Concentration

The percentage removal of the adsorbent was studied by varying Cr (VI) concentrations from 1 to 50 mg/L. The results of the study are displayed in Figure 8. The percent of Cr (VI) removal was increased as its concertation increased from 1 to 10 mg/L and then abruptly decreased as the Cr(VI) when concentration was increased above 10 mg/L. The increase in adsorption capacity with increasing initial concentration is because at a fixed adsorbent dose with increasing concentration of the adsorbate, all the available active sites of the adsorbent would be fully exposed to get occupied and thus, yielding a higher adsorption capacity [128].

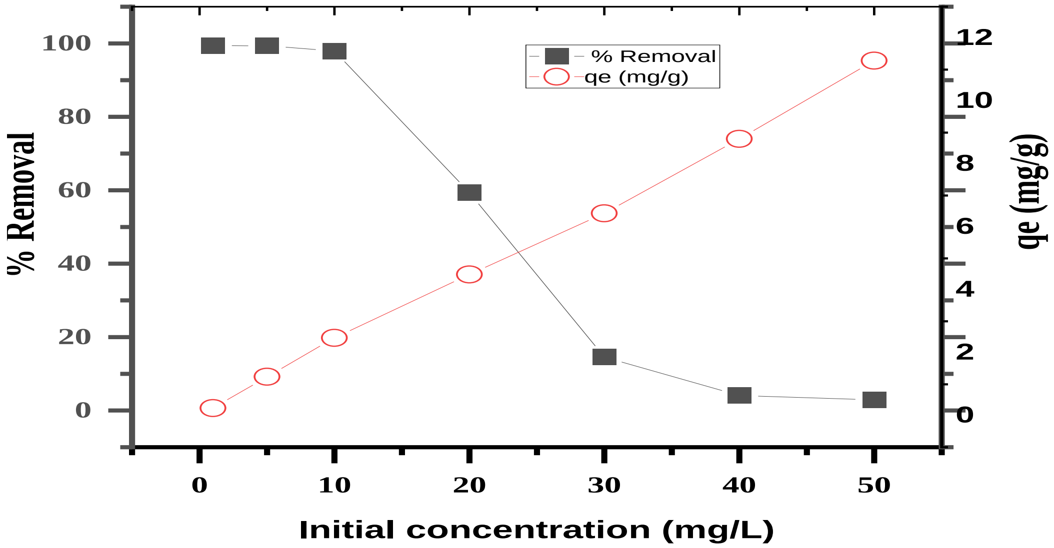

Figure 8: Effect of initial metal concentration on removal efficiency and adsorption efficiency: pH 2, Contact Time 3 hrs, Dose 5 g/L, rpm 200 and T 25^{o}C

4.4. Adsorption Isotherm Studies

The adsorption isotherm describes the mechanisms of the in-between the adsorbent and adsorbate. It is considered as a major factor for determining the adsorbent capacity and optimizing adsorbent consumption [129]. In this study, the Langmuir isotherm model and Freundlich isotherm models were used to describing the adsorption mechanisms of Cr (VI) on to ATRC adsorbent. Langmuir model describes monolayer sorption on distinct localized adsorption sites. It indicates no transmigration of the adsorbate in the plane of the surfaces and assumes uniform energies of monolayer sorption onto the sorbent surface [130]. Freundlich isotherm is used to describe adsorption processes that occur on heterogeneous surfaces and active sites with different energies based on multilayer adsorption and equilibrium [131].

Different concentrations of Cr (VI) including 1, 5, 10, 20, 30, 40 and 50 mg/L were used to investigate the adsorption isotherm. Figure 9 shows nonlinear Langmuir and Freundlich models. The obtained constants from the experimental data are presented in Table 4. The equilibrium separation factor is given in equation (14)

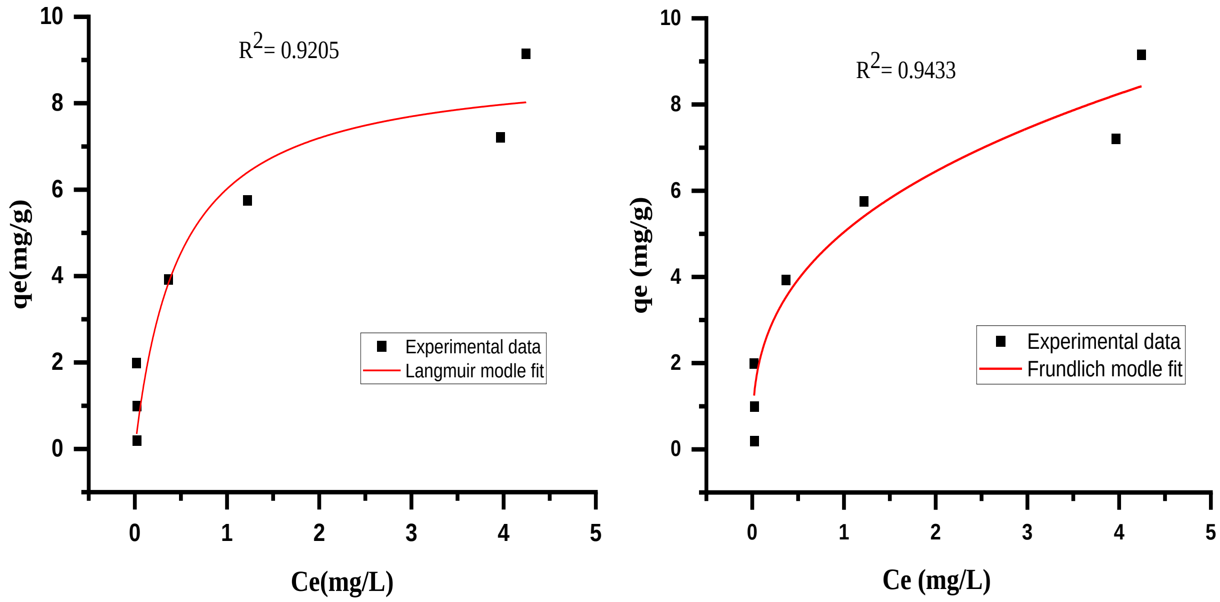

Figure 9: (a) Langmuir isotherm model and (b) Freundlich isotherm model for the adsorption of Cr(VI) onto ATRC

Langmuir's equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent [132]. The obtained R^2 value for this model was 0.9205 indicating that adsorption of Cr (VI) from aqueous solutions by ATRC is based on this model. The maximum adsorption capacity (q_m) obtained from Langmuir isotherm is 8.93 mg/g. The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor. The equilibrium separation factor is given in equation (15), the values of R_L indicate whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [133] The R_L value in this study is between 0 and 1 from the concentration range Cr (VI) (1- 40 mg/L), so R_L value indicated that the adsorption is favorable.

Freundlich isotherm is used for describing the multilayer adsorption with the reaction among the adsorbed molecules and also is effective for adsorption on heterogeneous surfaces. This isotherm is an exponential equation with the assumption that by increasing the concentration of the adsorbed mass, there is more amount of adsorption. The obtained R^2 value for this model was 0.9433, the Freundlich adsorption model constant (K_f = 5.0397) and the adsorption intensity (n = 0.355). In the Freundlich equation, the heterogeneity factor (1/n) is related to the capacity and intensity of the adsorption and "n" is a measure of the deviation from linearity of adsorption. Thus, when t 1/n is equal to 1, the adsorption is linear. For the values less than 1, the adsorption process is chemical, and if it is more than one, the adsorption will be a physical process. High surface heterogeneity occurs when the value of 1/n is near zero [134]. The value of 1/n in this study is 2.816 which is greater than 1 and thus, the adsorption is physical process.

In this study both the value regression coefficient R^2 and Chi-squared value (χ^2) were used to know the best model fit for the adsorption process. Based on the values of R^2, Freundlich isotherm better fit for the adsorption equilibrium data. This indicates that the adsorption of Cr (VI) by ATRC is evidently with multilayer and heterogeneous adsorption sites. The heterogeneity is caused by the presence of different functional groups on the surface, and various adsorbent–adsorbate interactions [135]. If model predicted data are very close to the experimental data, the value of χ^2 will be small and if they vary widely, χ^2 will be large [136]. χ^2 test result of Freundlich isotherm is lower than Langmuir isotherm, this indicates that the predicated data are very close to the experimental data in Freundlich isotherm, so Freundlich isotherm provides a better determination for the sets of experimental data.

Table 4: Langmuir and Freundlich isotherm constants for the adsorption Cr(VI) on ATRC

Isotherm	Parameter	Result
Langmuir	Qmax (mg/g)	8.9393
	b (L/mg)	2.0606
	R_L	0.0884
	R^2	0.9276
	X^2	1.0678
Freundlich	K_f ($(mg^{1-1/n}L^{1/n})/g$)	5.0397
	N	0.3255
	R^2	0.9433
	X^2	0.7620

4.5.Adsorption Kinetics studies

To investigate the mechanism of sorption such as mass transport and chemical reaction processes and to evaluate potential rate-controlling steps, the Pseudo-First Order model and Pseudo-Second Order kinetic model were studied. The experiments were performed by varying the contact time from 15 to 420 min, keeping the adsorbent dose, initial concentration and temperature constant. The non-linear plot of q_t vs t for pseudo first order and pseudo second order are presented in Figure 10a and 10 b, respectively

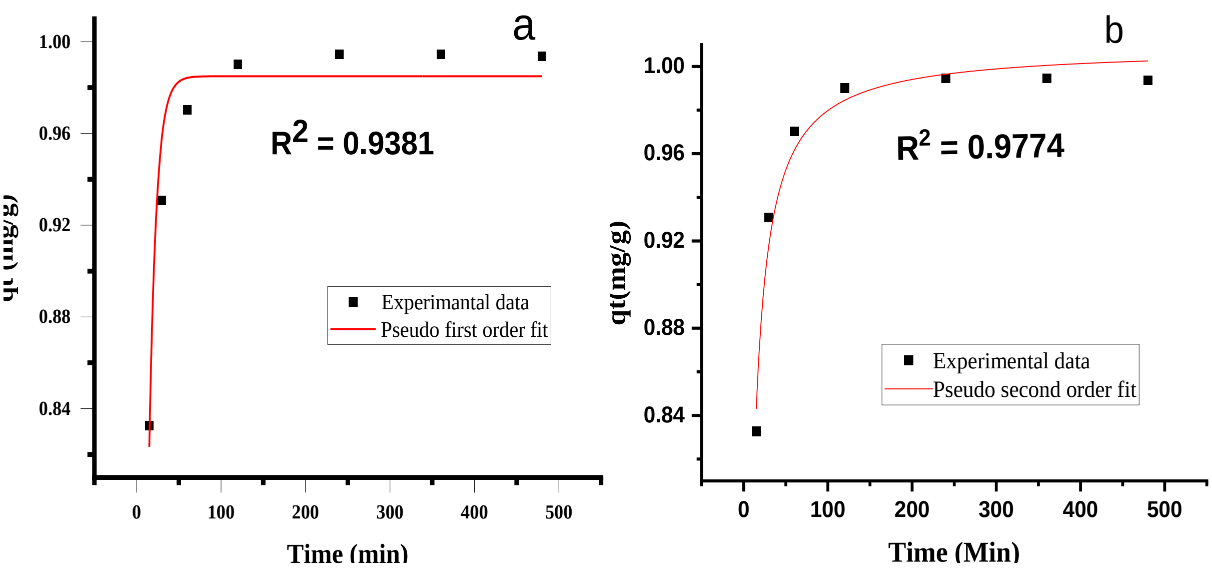

Figure 10: (a) Pseudo first order (PFO) and (b) Pseudo second order (PSO) plot for adsorption of Cr (VI) onto ATRC

The non- linear plot gave the value of kinetic parameters including first-order rate constant k_1, experimental and calculated equilibrium adsorption capacity, second-order rate constant k_2, and correlation coefficient (R^2), which are presented in Table 5. To evaluate the better fitting model, both nonlinear χ^2 and R^2 were used. For the Pseudo-first-order model, the obtained values of R^2, χ^2 and k_1 were 0.934, 6.7×10^{-6} and 0.1205, respectively. Whereas, for Pseudo-second-order R^2, χ^2 and k_2 0.9774, 9.73×10^{-5} and 0.336, respectively. Details of the experimental data are shown in Table 5. When, q_e(cal) and q_e(exp) were compared the two models have no significant differences.

Based on the R^2 values the pseudo-second order kinetics better fits the experimental data for sorption of Cr(VI) by ATRC. A better fit to the pseudo-second-order kinetic model indicates that the rate of adsorption is more dependent on the availability of the adsorption sites instead of the concentration in the solution [137]

Table 5: Parameters of the pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) adsorption

Parameter	PFO	PSO	Inter-particle diffusion
C_o (mg/L)	5	5	5
$q_{e,exp}$ (mg/g)	0.996	0.993	-----
$q_{t,\ cal}$ (mg/g)	0.984	0.983	1.51
K_1 (min^{-1})	0.1205	------	------
K_2 (g/(mg.min))	-----	0.3362	------
R^2	0.9381	0.9774	0.645
χ^2	2.6 x10^{-6}	9.73 x 10^{-5}	0.0015

Experimental data were assessed by intra-particle diffusion model to determine the rate controlling step and to find the adsorption mechanism. The presence or absence of intra-particle diffusion can be confirmed by applying the Morris Weber equation [106] expressed in equation (19). Figure 11 indicates intra-particle diffusion plots of Cr (VI) adsorption on ATRC.

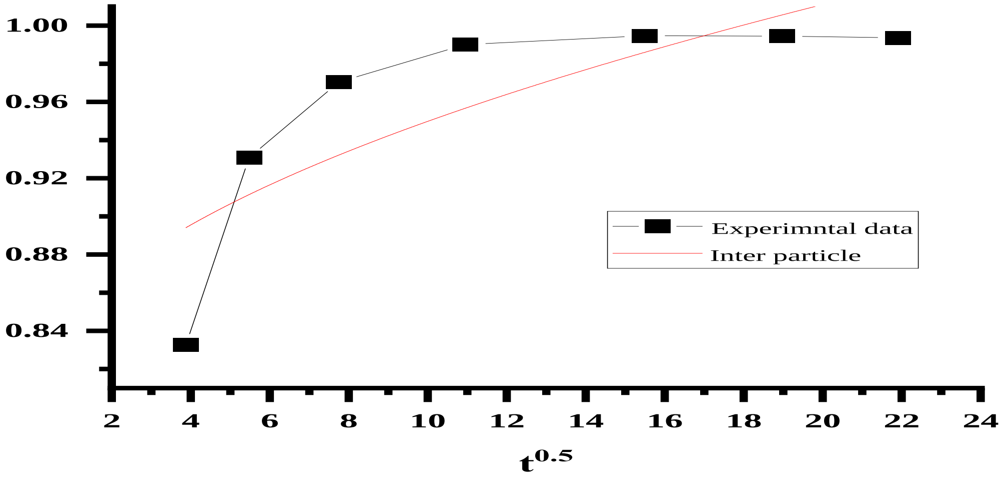

Figure 11: Intra-particle diffusion plots of Cr (VI) adsorption on ATRC

The adsorption process generally proceeds via three stages: (a) adsorbate transport from the bulk solution through the boundary layer onto the adsorbent surface (b) diffusion of adsorbate through the active pores; (c) intra-particle diffusion into the interior of the adsorbent [138]. According to this model if a plot of q_t vs $t^{0.5}$ is a straight line, the adsorption process would be controlled intra particle diffusion. If multilinear segments are appear in plots, two or more than two steps would control the adsorption process [139]. In the present study, the obtained results (Figure 11) showed the availability of different line segments in the plot of qt vs $t^{0.5}$ indicating that the intraparticle diffusion is not the only rate controlling step in the adsorption process.

4.6.Reusabilty Studies

The importance of adsorption process using biomass as an adsorbent is their low cost, availability on large scale and easy desorption of the adsorbed metal ions [140]. The adsorption and desorption capacity of Cr (VI) on the studied adsorbents are shown in Figure 12.Desorption tests were carried out using 1.0 M NaOH solution, 99.27% of Cr(VI) was removed in the first adsorption experiment. Then, after washing with 1.0 M NaOH, 74.56% of Cr(VI) ion was adsorbed. The percent removal Cr(VI) ion is decreased after washing with a desorbing agent because of the desorption effiency of desorbing agent and the amount of adsorbent may reduce during filtration

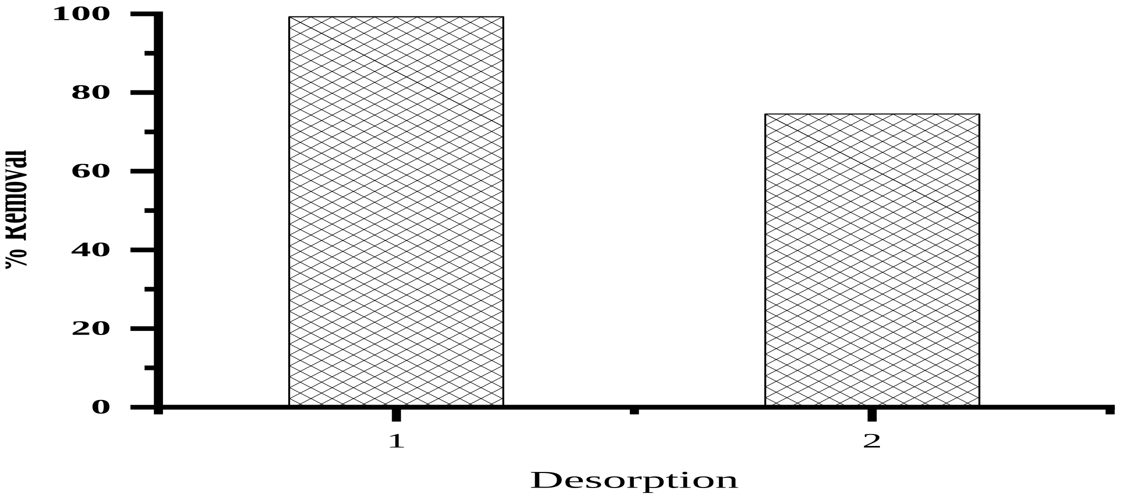

Figure 12: Desorption of Cr (VI) from the surface of ATRC with 1.0 M of NaOH

4.7. Comparison of Cr (VI) adsorption with other adsorbents

The adsorption capacity of ATRCfor removal of Cr (VI) was compared with different adsorbents are shown in Table 6. The adsorption capacity of ATRC was found to be 8.93 mg/g at 25 °C which is similar to some other reported adsorbents.

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

S/No	Adsorbent	pH	qe (mg/g)	Reference
1	Sawdust-activated carbon	3	3.46	Hamadi et al. (2001)
2	Peels of pea pod	2	4.33	Sharma et al., (2016)
3	Coaly activated carbon		8.77	Wu et al. (2009)
4	Ground nut shell	3	5.88	E. Pehlivan, et al(2008)
5	Activated rice husk carbon	2	0.8	Bishnoi, N et al, (2004)
6	Modified oak sawdust	3	1.7	Argun, M.E et al, (2006)
7	Almond shell carbon		10.6	Dakiky et al. 2002
8	Sawdust of Sal tree activated carbon	3.5	9.55	Baral, SS. et al (2006)
9	Sago waste activated carbon		5.78	Vennilamini et al. (2005)
10	Activated sugarcane bagasse	1	3.80	Adhena, A. et al (2014)
11	Sulfur acid-modified waste	2	7.49	Ghosh (2009)
12	ATRC	2	8.93	Present work

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this work, the use of ATRC adsorbent for effective removal of Cr (VI) from an aqueous solution was investigated. The Taro residue treated with concentrated H_2SO_4 was resulted in increasing in specific surface area of the adsorbent. Various operating conditions were optimized, and then the optimal conditions have been established. Accordingly, the optimal conditions were pH of 2, 5 mg/L initial metal concentration, 5 g/L of adsorbent dose and 180 min contact time. The active form of Cr (VI) that can be adsorbed onto the ATRC at lower pH is most likely $HCrO_4^-$. The investigated ATRC exhibited over 99% removal efficiency for Cr (VI). Moreover, the equilibrium adsorption data better fitted to Freundlich isotherm model which confirms the heterogeneous adsorption of Cr (VI) over activated taro residue surface and also the kinetics of adsorption data are fitted with the pseudo second order model. Moreover, desorption studies showed that the percentage of adsorbent reusability is promising to minimize secondary pollution.

Generally, according to experimental data presented in this work. ATRC can adsorb Cr (VI) from an aqueous solution. It may be concluded that activated carbon from Taro residue is used as a low-cost, effective, and alternative activated carbon for the removal of Cr (VI) from an aqueous solution.

5.2.Recommendations

Findings of the study have shown that, ATRC can remove Cr (IV) from aqueous solution> Based on the obtained results, the researchers want to forward the following

- A batch study is not enough to investigate the efficiency of a given adsorbent, and thus, we recommend column packing to determine the possibility of using ATRC as an adsorbent for the removal of Cr (VI), .
- It is recommended to evaluate the removal efficiency of the adsorbent for toxic industrial wastes such as dyes and other metals/\.

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