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Adsorptive removal of Cr (VI) onto Xanthated tea waste from aqueous solution

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Abstract

Removal of heavy metals is absolutely essential to avoid water pollution. In the present study, an efficient and cost-effective adsorbents was prepared by chemical modification of tea waste. The adsorbent was characterized by FTIR and XRD techniques. Batch adsorption experiments were performed in order to examine the removal process under various factors like the effect of initial concentration, adsorbent dose, pH, and contact time. The adsorption of Cr (VI) was found to be optimum at a contact time of 120 min, pH 2.0, and an adsorbent dose of 100 mg/L. The isotherm study revealed that the adsorption equilibrium was well-fitted to the Langmuir isotherm. The results showed that XTW was a favorable adsorbent of Cr (VI) from an aqueous solution.

Keywords: Adsorbent, Chromium(VI), Isotherms, Xanthated Tea Waste

Introduction

The environment is harmed by a variety of contaminants, both organic and inorganic. Heavy metal ions pose the greatest threat to the modern world because they are extremely poisonous and carcinogenic in nature. Heavy metal contamination is a product of human activity and the consequences for the ecosystem's food chain (Dhami & Homagai, 2020). Heavy metals are defined as metals with a high atomic weight and density. Fertilizer, manufacturing metal processing and Pulp and Paper manufacturing are examples of rapidly developing industries. The paper industry, mining activities, and the rubber-plastic sector are examples of industries that produce heavy metals in their effluents. Heavy metals such as cadmium, chromium, lead, Mercury, Nickel, and others are commonly found in industrial effluents, which pollute water bodies (Holmes et al., 2008). High levels of dangerous heavy metals including chromium, lead Mercury cadmium, and Cobalt have been discharged into the mainstream of our wastewater system as a result of growing industry and urbanization in our cities. The heavy metals are more stable and can have a negative influence on our ecology and public health if they are discharged into the environment without being treated (Malkoc & Nuhoglu, 2006). Heavy metals are non-biodegradable, bio-accumulative, and carcinogenic and have thus been linked to a variety of diseases and ailments (Holmes et al., 2008b). After air, water is nature's most crucial life-sustaining gift. It is impossible to overstate the importance of hazardous heavy metal ions in water bodies. The main sources of heavy metals in water bodies are geogenic and anthropogenic sources, with the latter being the most common (Sanchez-Hachair & Hofmann, 2018). Heavy metal pollution occurs as a result of fast industrial development.

Heavy metal-contaminated wastewater is discharged into the aquatic environment by industries such as electroplating alloy creation, leather industry tanning textiles dye and mining. Heavy metals are adsorbed by leaving creatures because they are non-biodegradable and soluble in water. They lead to accumulating in living species once they reach the food chain creating major health problems (Masekela, 2020). Because of their toxicity and other negative impacts on receiving water and soils, heavy metal ion pollution in the environment is a serious problem. They must be removed from wastewater before being discharged into the environment. Environmental guidelines are being established in order to keep a good check on the number of heavy metals released into the environment. The most stable form of chromium in the environment is hexavalent chromium and trivalent chromium. Chromium is a highly hazardous strong oxidant that can penetrate the skin. Due to its resemblance to sulfate in biological cell membrane structure chromium is, on the other hand, less poisonous and easier to work with. In low amounts, it is considered as micronutrient while at higher concentrations, it is considered a macronutrient. If concentrations are high enough they could be poisonous (Bayuo et al., 2019). Chromium in its hexavalent form is one of the most dangerous heavy metals known to have a wide range of human health impacts including mutagenesis and carcinogenic concerns. Chromium is used in the tanning of leather, the production of dyes and pigments, and the manufacturing of wood preservatives among other things.

Although there is no precise definition of what heavy metal is, density is frequently used as a criterion. Heavy metals are generally classified as those with a specific density greater than 5g/cm3. Exposure to heavy metals such as lead chromium Mercury and cadmium poses the greatest risk to human health. For thousands of years, heavy metals have been used in a variety of sectors. Lead has been utilized for at least 5000 years, with early uses including building materials and glaze color for pottery and water pipes (Kumar et al., 2020). Heavy metals can be categorized into two distinct categories; i) elements necessary for plant growth but harmful to humans such as copper iron Molybdenum nickel and zinc when their concentration exceeds particular levels in animals and plants. For some of these elements, the difference between recommended and hazardous amounts is fairly small: ii) elements such as arsenic cadmium Mercury and lead are not required by plants and animals (Kumar et al., 2020). Heavy metals are classified because of their atomic weight or high densities. The term heavy metal is now used to designate metallic chemical elements and meteorites. Toxic to both the environment and humans are metalloids. Some metalloids as well as lighter metals like Selenium, Arsenic, and Aluminum are toxic. Heavy metals have been labeled as such, albeit certain heavy metals are not. Gold, for example, is not usually poisonous. The following is a list of heavy metals bands ranked by the dear density of being greater than 5g/cm3 and are more commonly encountered in our daily lives (Chun et al., 2004)

Weathering of soil minerals, land application of treated wastewater sewage sludge and fertilizers and industrial operations are all sources of heavy metals in soils. Heavy metal not only does it pollute the land but it also has an impact on food product quality and safety. Some heavy metals are harmful to plants and extremely low amounts while others can accumulate in plant tissues to quite a high amount without causing any obvious symptoms or reduction in yield. Plants growing in heavy metal-polluted environments may experience changes in the metabolic physiological and biochemical process resulting in decreased growth and poorer Biomass production and metal accumulation. Heavy metals are taken up by plants and accumulate along the food chain posing a risk to animal and human health. The optic of nutrients by plant roots is one example of the main avenues for heavy metals to enter the food chain. Heavy metal absorption and accumulation in plant tissue rely on many factors such as moisture, organic matter pH temperature and nutrient availability. Heavy metal absorption is higher in the summer than in the winter (Shrestha et al., 2012).

People can be exposed to chromium via inhaling, eating, or drinking it, as well as through coming into touch with chromium or chromium compounds on their skin. Chromium levels in the air and water are normally low. Chromium level in drinking water is typically modest however contaminated well water may contain the Deadly chromium; Hexavalent chromium. Chromium is a natural element. Because very minute levels of chromium are required for human health; it is referred to as an essential trace element. Chromium is divided into two types; foods and supplements containing trivalent chromium are safe for humans. Trivalent chromium is an essential component for humans; a deficiency can lead to cardiac problems, metabolism problems, and diabetes. However, too much chromium could have negative health consequences such as skin rashes. Hexavalent chromium is toxic to humans, especially those who work in the steel and textile industries. People who consume cigarettes are more likely to be exposed to chromium. There are various types of chromium each with its own set of impacts on living things. Natural processes and human activities introduce chromium in the form of trivalent chromium and hexavalent chromium into the air, water, and soil.

The zero trivalent and hexavalent states are the most important in commercial products and the environment, even though they exist in numerous Oxidation States. The trivalent state of chromium is found in nearly all naturally occurring chromium, frequently in conjunction with iron or another metal oxide (emerald-green et al., 2019).

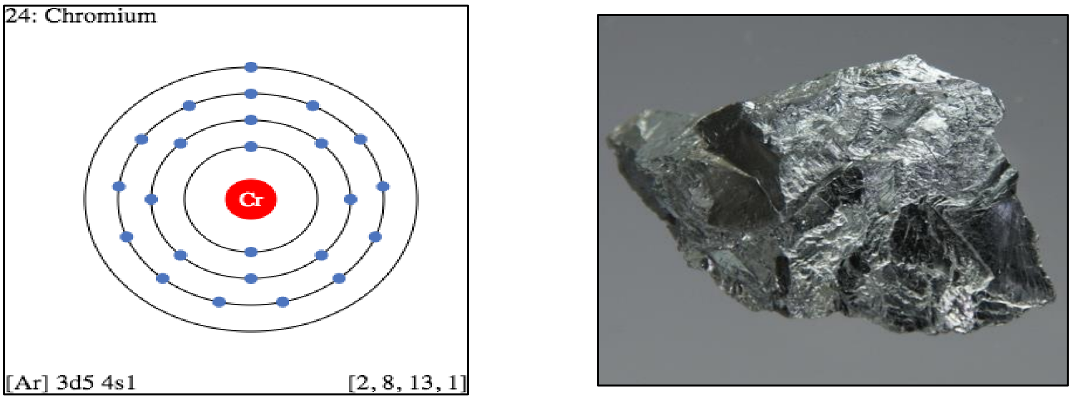

Figure 1. Electronic configuration of chromium

Chromium compounds are used as industrial catalysts and pigments. Rubies get their red color from chromium and glass treated with chromium has an emerald green color. After Oxidation State + 3, Oxidation state +6 is the second most stable oxidation state of chromium. Exam Island chromium in acidic media forms the bright orange dichromate $_4$ion ($Cr_2O_7^{--}$) and in alkaline media the bright yellow chromate ion (CrO_4^{--}) is formed. The dichromate ion is a strong oxidizing agent, the chromate ion much less so. A well-known and very precise test for either dichromate or hydrogen peroxide is the formation of the deep blue peroxide CrO_5. Chromium can also exist as an extremely volatile liquid with an orange/ brown vapor in its plus 6 Oxidation State. This substance is known as chromyl chloride and has the formula CrO_2Cl_2. Chromium can exist in an aqueous solution in the +2,+3,+5, and +6 Oxidation States (Sameera et al., 2011).

The environment refers to the physical environments in which humans, plants, animals, and my groups live or operate. It is made up of three elements: land, atmosphere and water. The four spheres that make up the earth's system are the biosphere (living things), the atmosphere (air), the lithosphere (land), and the hydrosphere (water), all of which function in Unison. Contaminants in the environment often known as pollutants are compounds that are present in higher concentrations than in any other parts of the environment. Several pollutants such as inorganic ions, organic pollutants, oregano metallic compounds, radioactive isotopes and gaseous pollutants have severely damaged the environment. Among these Pollutants, heavy metals are deadly poisonous for our environment as well as living beings (Briffa et al., 2020). Since the earth's origin, these heavy metals have been found naturally on the earth’s crust. Because of the astounding increase in the use of heavy metals in different sectors, has resulted in an imminent surge of metallic substances in both the environment; terrestrial and aquatic. Heavy metal pollution has evolved as a result of an entheogenic activity which is the primary source of pollution. Mostly owing to metal mining, smelting, and other industries that are based on metal, leaching of metal from different sources such as landfills, waste dumps, excretion, livestock, and chicken manure, runoff automobiles, and road construction. The use of pesticides, insecticides, fertilizers and other heavy metals in agriculture has been a secondary source of heavy metal contamination. Heavy metal contamination can also be caused by natural events such as volcanic eruption metal corrosion metal evaporation from soil and water and sediment re-suspension, soil erosion, and geological weathering. Happy metal toxicity Rises as a result of the concentration of a large amount of the metal in one place. Heavy metals cannot be broken down since they are non-biodegradable and hence exist in the environment for a long period. In presence of other elements in soil or sediment, they can react and form or degrade making more poisonous compounds. Farmers sometimes combine sewage sludge with soil; however, this can contain heavy metals especially if the sludge was created by industries. Heavy metals such as copper zinc lead cadmium and chromium have been identified in high concentrations in the soil of these agricultural regions (Alissa et al., 2011). All metals in excess can be a source of sickness. Excess and lack of critical metals can have a negative effect on the human body. Inhibition of enzyme activity Protein synthesis changes in nucleic acid function and changes in cell membrane permeability are all examples of toxicity processes of heavy metals. Metals with hazardous or carcinogenic qualities can interact with nuclear protein and DNA causing oxidative degradation of biological macromolecules. Some metals can form reactive radicals which can cause DNA damage, lipids peroxidation and protein depletion. Neurotoxicity, hepatotoxicity, and nephron toxicity are all side consequences of metal toxicity (Alissa et al., 2011). Heavy metals have sparked a lot of debate about their use because of dear harmful consequences.

MutaGenesis chromosomal fracture, carcinogenesis, and pulmonary toxicity have all been reported as the harmful effects of heavy metals. These heavy metals directly or indirectly affect living beings and the ecological harmony of our environment. Therefore, focusing on specific methods and technology to remove heavy metals from different kinds of effluents discharged from different industries is necessary. Because of the toxicological effects of heavy metals on the environment animals and humans, it is critical to treat wastewater effluent before they are discharged into the environment. Heavy metals are hazardous because they can cause chronic degenerative changes in the brain system, liver, and kidney as well as teratogenic and carcinogenic consequences in some situations. Although enzymatic inhibition decreases antioxidant metabolism and oxidative stress may play a role, the mechanism of toxicity of some heavy metals is yet unknown. The fact that these metals are in the top ten on the current agency for toxic substance and disease registry priority list of hazardous substances demonstrate their importance as environmental health threats. This list is best on the substance's toxicity as well as the possibility of contamination in the air, water, or soil. These metals and their compounds have been widely diffused in the environment as a result of their widespread use in industrial and consumer products. To account for probable chemical contamination maximum values for heavy metals in food have been established. The Centers of Disease Control (CDC), the World Health Organization (WHO), the Occupational Safety and Health Administration (WHO-OSHA), the International Program on Chemical Safety (WHOIPCS), the Joint FAO/WHO Expert Committee on Food Additives (JECFA), and the International Agency for Research on Cancer (IARC) have all evaluated the toxicity of heavy metals (Ashour & Tony, 2020).

Removal methods

Possible methods of removal of hexavalent chromium from wastewater effluents include the chemical adsorption process is versatile in terms of design and operation and it produces high-quality treated effluent in many cases. Adsorbents can also be renewed using an appropriate desorption procedure because adsorption is sometimes reversible. Adsorption is a phenomenon that occurs when a gas or liquid solute gets accumulated on the liquid or solid surface forming an adsorbate film because of physical and chemical interactions. Absorption is a surface phenomenon. Adsorption can be divided into two categories; physical and chemical adsorption (Labied et al., 2018). Physical adsorption is also known as physisorption and is due to weak Vander Waals force between adsorbent and adsorbate. Chemical adsorption is also known as chemisorption and is due to the strong chemical bonding force between adsorbent and adsorbate. Physisorption is a multilayered phenomenon whereas chemisorption is a monolayered phenomenon. Adsorption is affected by various factors such as; temperature, pH, pressure surface area of adsorbent, etc. We can break solid crystals into little pieces by heating charcoal at high temperatures breaking lumps of solid into powder and other procedures suitable for the adsorbent can all be used to increase the number of unoccupied sites on precipitation Ion exchange method, absorption, membrane filtration reverse osmosis, coagulation and flocculation, flotation, electrochemical treatment chemical reduction method solvent extraction evaporation method, etc. However, most of these approaches resulted in incomplete metal ion removal Limited selectivity, high operational cost, high energy and reagent used, and secondary pollution creation. Furthermore, it was discovered that when these approaches are used some of them fail to reach the discharged regulatory limits for heavy metals concentration ranging from 0.1- 3mg/L.This adsorption method is now widely accepted as a viable and cost-effective approach to heavy metal wastewater treatment. In worldwide environmental protection regions, the adsorption technique is still the most effective and extensively utilized technology. Reusability, cheap operational cost selectivity for specific metals, fast operational time and no chemical sludge are all advantages of adsorption over traditional processes. Plant seeds, pomegranate peels, orange peels, and other agricultural materials have been utilized to absorb heavy metals as mentioned in numerous research. The bio adsorption process is attractive due to its widespread availability at low cost or no cost, and strong performance in extracting heavy metals from aqueous solution.

Several treatment processes have been developed over the years to remove heavy metals contained in industrial wastewater including chemical precipitation Ion exchange membrane filtration river osmosis and others. However, most of these approaches have drawbacks as lengthy treatment processes, expensive costs, and significant energy usage. Because of its large surface area, high adsorption capacity and a high degree of surface reactivity, activated carbon is a prominent adsorbent in the adsorption process. It is necessary to regenerate it after each adsorption experiment and because it is costly scientists endeavored to research inexpensive and efficient adsorbent materials in order to reduce the cost of the treatment process. The use of inexpensive readily available and ecologically friendly biomaterial for the removal of heavy metals from aqueous solution has been investigated and reported on. The inclusion of functional group search as amino phosphate Carboxylic, hydroxyl, and sulfate groups in these biomaterials has been related to their high adsorption capacity. Bio-adsorbent is inexpensive material that has a high affinity and binding capacity for metals and is widely available. Those adsorbents having sulfur-bearing groups have a high affinity for heavy metals but a poor affinity for light metals (Sanchez-Hachair & Hofmann, 2018). Because of certain advantages of the adsorption method in comparison with other methods such as easy removal of contaminants technologically simple and adaptability to many treatment formats, working at mild operation conditions and at a wide pH range process does not produce any toxic by-product requires low investment a wide range of a product can be used as an adsorbent, it can be used for a wide variety of target contaminants, scientists are investigating and conducting research for more information on the adsorption process. Because of all reasons mentioned above, the adsorption method for the removal of heavy metal became a choice of many researchers (Kaur et al., 2017).

Bio-material for Adsorption

Rapid industrialization and insufficient effluent treatment systems in many industries are resulting in a massive amount of low-quality water entering aquatic bodies. The presence of heavy metals is one of the factors that influence water quality. The existence of heavy metals could create crucial problems in living organisms and ecology. For the removal of heavy metal from effluents different techniques were developed. The comparatively adsorption process is a somewhat efficient method of removing heavy metals, organic contaminants and inorganic debris from polluted streams. Because of its large surface area and high adsorption capacity coal based carbon is the most often employed adsorbent. Although utilizing a coal-based carbon adsorbent to remove contaminants from water is successful the high cost has prompted researchers to look for other and less expensive adsorbents. Currently, The Hunt for low-cost adsorbents to remove pollutants from wastewater is intensifying. It has been verified by various researchers that bio adsorbents from various agricultural waste or byproducts are the Great contestant as precursors to remove the heavy metal ions from effluents (Meena et al., 2008).

These adsorbents are very economical eco-friendly are renewable cheaper with excellent heavy metal removal ability and are widely available. Many researchers have already attempted to make bio-adsorbent from agricultural waste such as banana peels, plum kernels, nutshells, tea leaves, sawdust, wheat bran, coffee grounds, coconut husk, jackfruit peel, and rice husk for the removal of heavy metal from wastewater. It is highly advised that these be used as bio-adsorbent precursors to help alleviate the problem of solid waste disposal while also generating local revenue. Similarly, many other locally available waste materials and byproducts can be widely used as adsorbents. In our study xanthated tea waste has been used as abio-adsorbent for the removal of Cr (VI) from an aqueous solution. The effectiveness of the adsorbent was studied by determining the maximum adsorption capacity using the batch method.

Figure 2. Tea leaves

Figure 3. Tea powder

Significance of Bio-adsorption

Bio adsorption is the process of removing metals, nonmetals and small particles from a solution using any biological component. Cellular products and leaving and nonliving Biomass can be used for effective adsorption but their cost-effectiveness and reusability factors remain under question. Metal ions can be removed from an aqueous solution using a variety of physical, chemical and biological processes. Many biological materials have a high eradication rate for reducing heavy metal concentration from ppm to ppb. Few types of bio-adsorbent bind to heavy metals with no Preference whereas others are selective for certain metals. Because of this reason, bio-adsorption Research and studies have become one of the busiest study fields. Bio-adsorbent made from agriculture and animal wastage is of great interest.

However, selecting a bio-adsorbent for a certain metal is a difficult task that requires a hit-and-trial method based on a series of experiments and expensive research. The current Technology for removing metal ions from wastewater is too expensive. They include I will exchange resins, solvent extraction electrolytic and precipitation process electro dialysis, and membrane technology. Due to the high capital investment required these techniques are not economically feasible for small-scale Enterprises seen in underdeveloped countries (Shrestha et al., 2016).

Bio adsorption is unaffected by Cellular metabolism. In the literature, bioabsorption is described as an efficient and selective process. Bio absorption can be done at a pH range of 3-9 and temperature ranging from 4 to 90°C. Because the ideal bio-adsorbent particle size is between 1 and 2 mm, both absorption and desorption equilibrium is reached quickly. The operating cost of this method is low as this method does not necessitate a large initial investment. Furthermore, biological materials are frequently low-cost and can be sourced from agriculture or industrial waste. The following are some of the fascinating advantages of biosorption over conventional treatment methods: low cost, high efficiency, minimal chemical, and biological sludge, no additional nutrition demand, biosorbent regeneration, and metal recovery (Sameera et al., 2011).

A wide range of bio-materials available in nature have been employed as biosorbents for the desired pollutant removal. Most of the biosorbents employed were made up of dead biomass, which has several advantages over using living microorganism metal ion loaded biosorbents can be easily desorbed and reused, dead cells may be easily kept or used for longer periods, dead biomass is not subject to metal toxicity constraints, nutritional supply is not required. A wide range of target sorbents has been removed from aqueous solution by the application of bio adsorbents including heavy metals dyes, fluoride, phosphate, pharmaceuticals, etc.

Despite this, most bio-sorption research has concentrated on the removal of metal ions and associated elements such as actinides, lanthanides metalloids, and their radioisotopes ions (Ruthven, 1984).

Bio-adsorbents are made from naturally plentiful waste biomass that is also cost-effective. They have a high adsorption capacity and can be reused once the metal ions have been desorbed. For the removal of heavy metals from wastewater many researchers have looked at new biosorbents such as sugarcane bagasse, orange waste, sawdust, olive stone, seaweeds, wheat straw, and chitin. The present study was conducted to utilize tea waste as efficient alternative adsorbent material to remove Cr (VI) from an aqueous solution using the batch method. The influence of operating conditions such as pH, adsorbent dose, initial concentration, and time of contact was studied.

General Objective

Preparation of xanthate tea waste from raw tea waste and the investigation of its adsorption capacity for the removal of Cr (VI).

Specific Objectives

- Preparation of raw tea powder from tea waste.
- Charring of raw tea powder using concentrated sulphuric acid.
- Xanthation of charred tea powder using sodium hydroxide and carbon disulfide.
- Study of physicochemical characterization of xanthate tea powder.
- Study of the kinetic parameter of xanthate tea powder.
- Study of various isotherm models for the best fit of the isotherm.

Materials and methods

All the experiments in this study were carried out with chemically xanthate tea waste collected from a local market in Lainchaur, Kathmandu, Nepal. And the chemicals used for this research work were used of LA/AR grades without further purification.

Instrument Used

- UV-visible single-beam spectrophotometer (SPECTRO UV-2510TS)
- UV-visible double beam spectrophotometer (LABTRONICS,Modellt-2802)
- Electric balance (Machine number: 038943)
- Hot air oven (ELITE OVEN)
- Auto Deluxe pH meter (Model:LT-10)
- Rotary Flask shaker
- Magnetic stirrer (LABINCO-L34)
- Sieve (NEW DELHI-110055)
- Mortar and pestle
- FTIR-spectrometer (PerkinElmer)

Preparation of Reagents

Preparation of 1000 ppm Chromium (VI) solution

A stock solution of Cr (VI) was prepared by dissolving 1.414 grams of $K_2Cr_2O_7$ in a 500ml volumetric flask and adding distilled water to give a 1000 ppm solution. Other working solutions of Cr (VI) were prepared by diluting the stock solution in distilled water.

Preparation of 1M Sodium hydroxide (NaOH) solution

40 grams of NaOH pellets were added in a 250 ml volumetric flask and distilled water was added up to the mark level to make 1M NaOH solution and it was further diluted as per the requirements.

Preparation of 1M Hydrochloric Acid (HCl) solution

16.02 mL of conc. HCl was taken in a 250 mL volumetric flask and then distilled water was added up to the mark level and was shaken vigorously thus the prepared solution was further diluted as per the requirement.

Preparation of Buffer Solution

- Buffer solution pH 4.0

The buffer tablet of pH 4 was dissolved in 100 mL of distilled water in the volumetric flask.

- Buffer solution pH 7.0

The buffer tablet of pH 7 was dissolved in 100 mL of distilled water in the volumetric flask.

Preparation of Adsorbent from Raw Tea Waste

Raw tea waste was collected from the local tea shop situated at Lainchaur, Kathmandu, Nepal. It was then sun-dried for 3-4 days to remove moisture from the tea waste. After completely dried it was taken for further process in the laboratory and thus adsorbent was prepared.

Preparation of Charred Tea Waste Adsorbent (CTW)

500 grams of dry raw tea waste was taken in a 4-liter bucket and conc. H_2SO_4 was added and stirred with a wooden spatula until it turned to completely black color. Then it was left for 24 hours with occasional stirring with a wooden spatula and thus a complete reaction took place. The process is hence called the charring process. In this charring process the ring opening of cellulose takes place. The charcoal formed was soaked in rainwater for more than 24 hours. Again, the charcoal was washed several times with rainwater. Further, the sample was washed with distilled water and the sample was completely neutralized up to pH 7 and was left for shade dry. After 3-4 days of shade drying it was dried in an oven for 6 hours. The dried charcoal was

grinded and sieved with 150 micrometers. Finally, the charred sample of tea waste got ready and was kept in an air tight bottle.

Preparation of xanthate tea waste (XTW)

100 grams of the CTW was added into the 300 mL of 15% NaOH solution and shaken for two hours. Further 20 mL of CS_2 was added and stirred for 3 hours then left overnight. It was filtered and washed repeatedly with rain water until the pH of the suspension became neutral. Then it was kept in the shade dry. After 1-2 days of shade drying, it was kept a in a hot air oven at 80 degree Celsius to make it completely dry and finally, It was kept in air tight bottle. This material is ready for the experiments and is called xanthate tea waste (XTW).

Characterization of the adsorbent

To enhance the adsorption capacity of the tea waste, it was chemically modified with different chemicals sulphuric acid, sodium hydroxide, carbon sulfide, etc. The main aim of this project work was to develop a noble, low-cost adsorbent from tea waste modified by Chemical treatments for the effective removal of Cr(VI) from the aqueous solution. The tea waste was characterized by using Fourier Transform Infrared Spectrometer to determine the functional groups on the adsorbent. Characterization of tea waste was done before and after the metal ion adsorption.

FTIR Analysis

The IR spectra of the xanthate tea waste before and after Cr(VI) adsorption were obtained to determine the possible involvement of the functional group present in the xanthate tea waste on the adsorption process. The FTIR spectrum of Raw Tea Waste (RTW) and Tea Waste (XTW) before and after the adsorption of Cr(VI) was carried out in the laboratory of Amrit Campus, Lainchaur, Kathmandu, Nepal. In infrared spectroscopy, IR radiations were passed through a sample. Some of the IR radiation was absorbed by the sample and some of it was transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. The FTIR approach is an important tool for identifying some characteristic functional groups which can adsorb the heavy metal. The effects of the presence of the surface functional group on the adsorb heavy metal were analyzed by observing the shifting of the FTIR peaks before and after the adsorption experiment.

Adsorption Study

The adsorption study was done with a prepared working solution of Cr(VI) and adsorbent prepared from raw tea waste that is xanthate and investigated the effect of initial concentration of metal ion, pH of the solution, contact time, effect of dose and effect of temperature of the adsorption process. Most of the chemical used in this study were LA/AR grades and were fresh. The working solution of various concentration required were prepared by diluting the stock solution. For the diluting purpose distilled water was used. The pH of the solution was maintained by using hydrochloric acid and sodium hydroxide of different concentrations. 25mL of chromium solution was taken in a reagent bottle and 0.2 grams of prepared adsorbent was poured into it. It was equilibrated in a mechanical shaker for 6 hours at room temperature. The equilibrate solution was filtered using filter paper and the filtrate was used to analyze the remaining concentration of Cr(VI). Firstly, absorbance before and after adsorpt was determined by using a UV- visible spectrophotometer. After that concentration before and after adsorption were calculated.

Effect of pH

The adsorptive removal of metal ions from an aqueous solution is dependent on the pH of the solution as it affects the surface charge of the adsorbent, the degree of ionization, and the species of the adsorbate. Batch adsorption tests for Cr (VI) removal were carried out to examine the adsorption behavior onto xanthate Tea Waste (XTW). In the test, pH studies were performed by shaking 25mL of Cr (VI) solution of known concentration that is 50 ppm containing 0.2 grams of each xanthate tea waste in the reagent bottle. To study the effect of pH on the chromium removal efficiency the pH of the solution was varied from 2 to 10. Each bottle was then agitated in a mechanical shaker at room temperature 170-180 rpm for about 5-6 hours to attain equilibrium. The equilibrium pH of the solution was measured by using a digital pH meter and recorded. The filtrate was used for measuring concentration. The pH affects the solubility of metal ions and the ionization state of functional groups, such as carboxyl, phenols, hydroxides, amino groups, and hydrocarbons of the cell wall. The pH value of 2.0 was taken as the optimum pH.

Effect of Adsorbent dose

Adsorbent dose seems to have a great influence on the adsorption process. The effect of the adsorbent dose on the adsorption process can be carried out by preparing the adsorbent-adsorbate solution with the different amounts of adsorbents added to fix the initial Cr (VI) concentration and shaking together for 6 hours. Different studies show that the amount of adsorption increased with increasing the amount of adsorbent dosage. The heavy metal removal efficiency of adsorbent is directly related to the number of available adsorption sites. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in, and hence the number of ions bound to the adsorbent and the number of free ions remains constant even with further addition of the dose of adsorbent. For lower values of adsorbent dose, there was an increase in the percentage removal of Cr (VI). The amount of adsorbent added to the solution determines the number of binding sites available for adsorption. The decrease in the sorption capacity with the increasing adsorbent dose suggests that at the constant concentration on increasing sorbent amount, the number or binding sites increases. Thus the effect of adsorbent dosage on percentage adsorption and uptake is an important parameter.

Effect of initial Cr (VI) concentration

The study of adsorption isotherms indicates the adsorption capacity of the adsorbent at experimental conditions. The adsorption isotherm is a plot that relates the amount of adsorbed per unit mass of adsorbent to the amount of unabsorbed adsorbate remaining in a solution at equilibrium time. Though the adsorption of metal ions increases initially with an increase in equilibrium metal ion concentration, several methods have been developed to describe the adsorption system, and the behavior of heavy metals. An Isotherm study was carried out with different initial concentrations of chromium ranging from 50 ppm to 700 ppm with an adsorbent dose of 0.2g at optimum pH 2. The solutions were equilibrated for 5-6 hours and Cr (VI) absorbance of xanthate tea waste before and after was absorbed using UV visible spectrophotometer. Hence, using absorbance, the concentration of before and after adsorption of xanthate tea waste was calculated.

Effect of contact time

Contact time is another important factor that affects the efficiency of metal uptake in batch adsorption processes. The investigation was done to determine the optimum time for the adsorption of Cr (VI) using xanthate tea waste. The influence of the contact time for the removal of Cr (VI) from the aqueous solution using the adsorbent was analyzed under keeping the other parameters constant. The effect of contact time on the adsorption of Cr (VI) was carried out by preparing the adsorbent adsorbate solution with a fixed adsorbent dose and initial Cr (VI) concentration for different time intervals (10-180 min) and shaking them together. The contact time required to attain equilibrium is dependent on the initial concentration of the pollutants. The percentage of removal increases with time until equilibrium is attended.

Effect of temperature

Temperature is another crucial parameter in the adsorption process. According to the adsorption theory, adsorption decreases with an increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperature. In this study, the effect of temperature was performed at three different temperatures in a thermostatic shaker machine while keeping all other parameter constants (optimum contact time, pH, adsorbent dose, and initial concentration). The adsorbent-adsorbate solutions were agitated with a fixed speed of 170-180 rpm, and the mixture was filtered and filtrate analyzed for the residual metal ion.

Kinetics study of Adsorption of Chromium (VI)

Adsorption kinetic was studied to evaluate the efficiency of adsorption. The adsorption kinetics of the adsorption process was analyzed using the pseudo-first-order and pseudo-second-order kinetic models. After evaluating the optimum pH adsorbent dose and initial concentration, the equilibrium time of the adsorbent of Cr (VI) was investigated at the optimum pH value at room temperature to determine the equilibrium time. Kinetic studies were carried out by shaking 0.02 gram of adsorbent with 25mL of solution of known concentration 50 ppm for xanthate tea waste. The absorbance before and after adding adsorbent was taken by using a UV visible spectrophotometer. In a reagent bottle, each with 0.2g adsorbent of xanthate tea waste was shaken in a mechanical shaker for 10 min, 20 min, 30 min, 60 min, 90 min, and 180 min respectively. The sample was collected and then filtered and then analyzed. The absorbance of the chromium before and after was determined by using a UV-visible spectrophotometer.

Results and discussion

X-ray Diffraction (XRD) Analysis of Adsorbents

In the figure below XRD patterns for RTW and XTW show weak and unresolved peaks, indicating amorphous nature. The amorphous nature of the biosorbent made its use in biosorption possible, which allows the metal ions to penetrate the surface rapidly. Reddy et al claimed that the bio absorbents amorphous nature is due to a high content of lignin, cellulose, and hemicelluloses. There is no notable difference between the XRD patterns of Tea waste before modification and after modification forming adsorbents such as RTW and XTW.

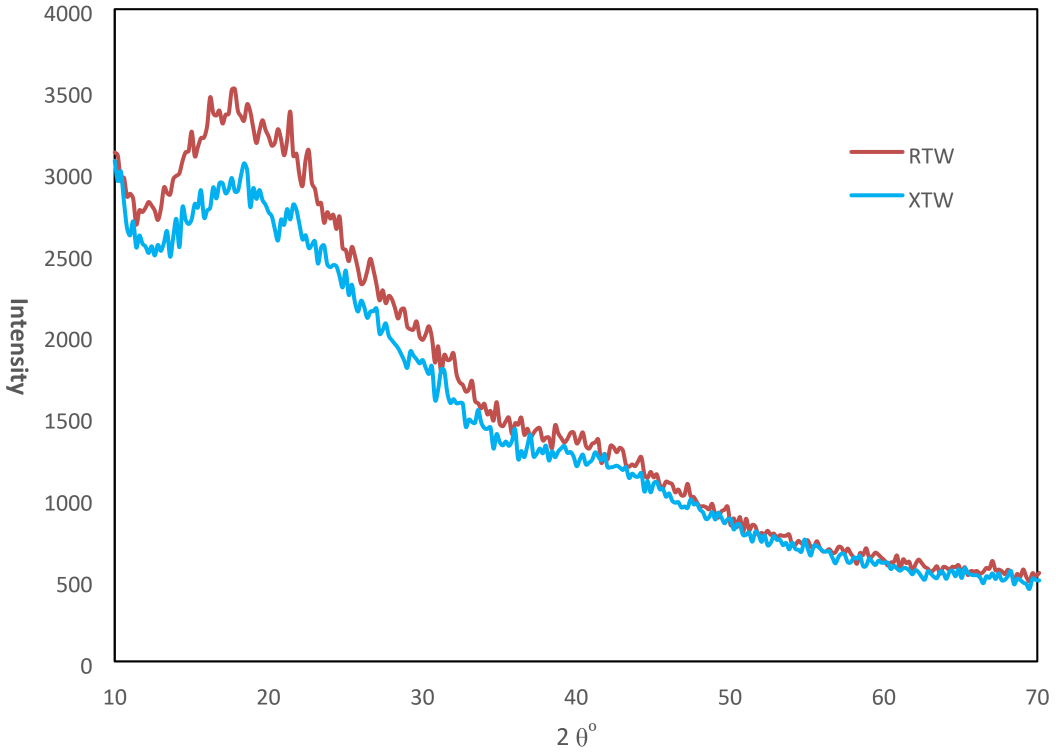

Figure 4. X-ray diffraction patterns of RTW and XTW

FTIR analysis

The FTIR spectrum of RTW and XTW are shown in the following figure separately. The FTIR spectrum of adsorbents was taken between 300-4500 per centimeter (cm^{-1}) using an IR tracer. By the close inspection of the FTIR spectrum, the sample showed a clear peak at 2930 cm-1 which can be assigned to the C-H group. The peak around 1209 cm^{-1} is characteristic of the C-O group. The stretching vibration of C=O and C=C found at 1627 cm^{-1} and 1700 cm^{-1} respectively.

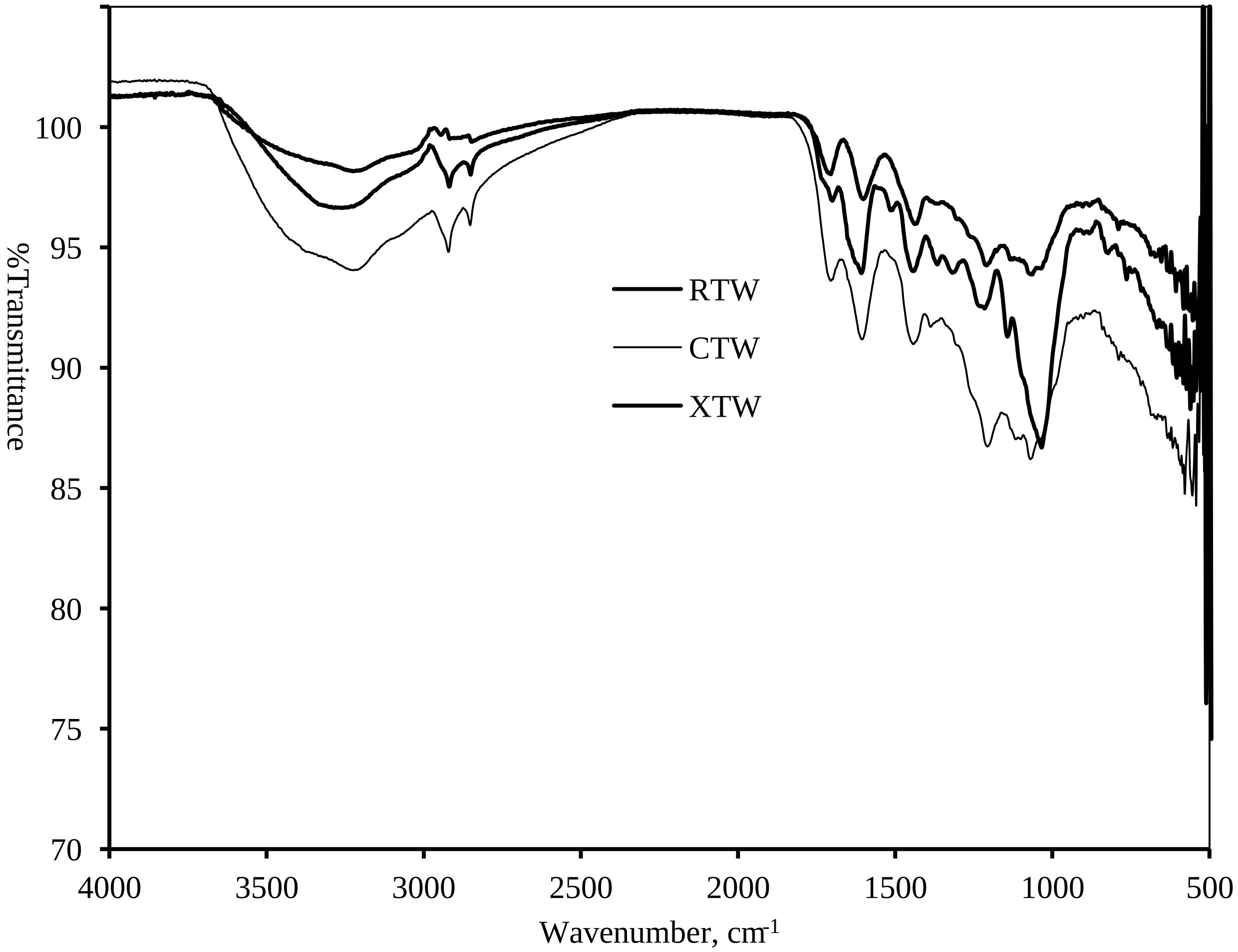

Figure 5. FTIR spectra of RTW, CTW and XTW

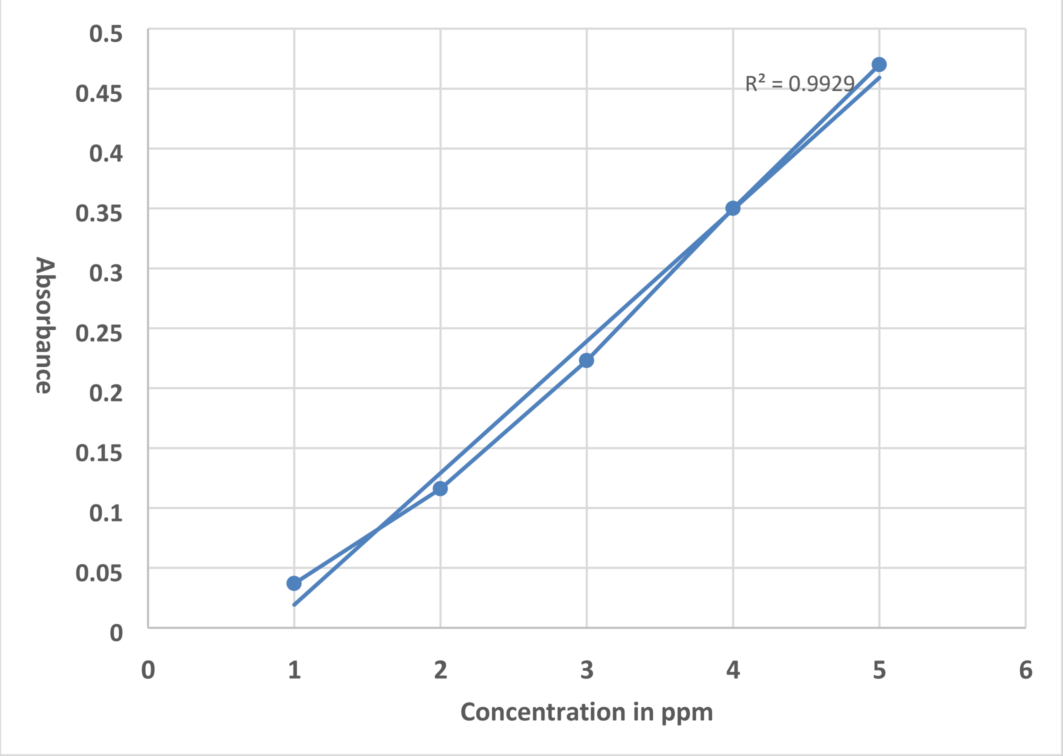

Figure 6. calibration curve

Effect of pH

The above figure shows the effect of pH on the adsorption of Cr (VI) onto xanthate tea waste at an initial concentration of 50 ppm at room temperature. The pH of the solution has a significant impact on the uptake of chromium metal since it determines the surface charge of the adsorbent and the degree of ionization of the adsorbate. In order to establish the effect of pH on the biosorption of chromium metal, the effect of pH at a different value between 1.0-7.0 for xanthate tea waste with chromium metal was carried out. The percentage removal of chromium metal by xanthate tea waste increased from 50.39% - 82.29% and then again decreased when the pH of the chromium solution increased from 1.0 to 7.0. From studies, the optimum pH for the XTW was found to be 2.0. The adsorption increases rapidly near the optimum pH range.

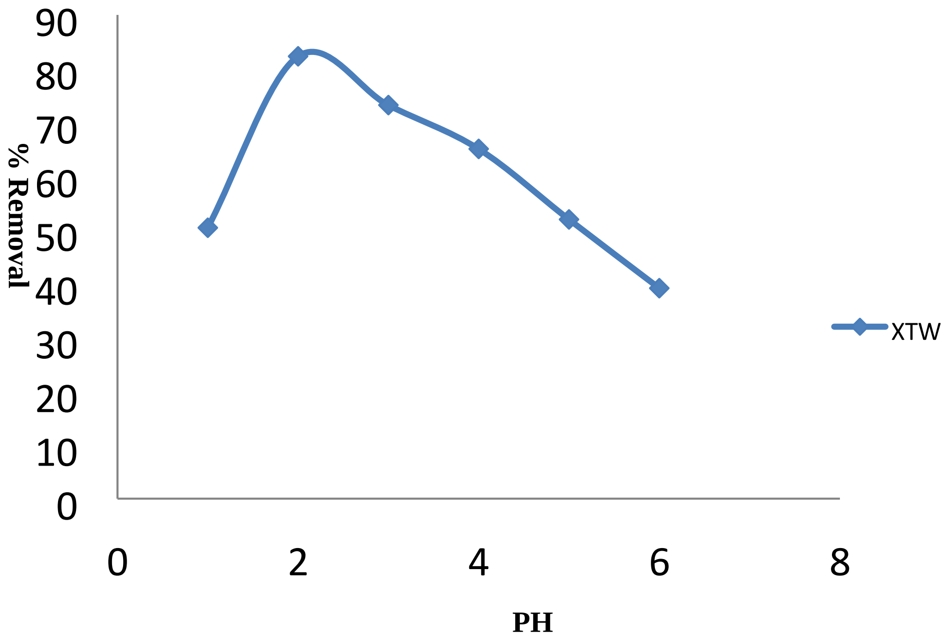

Figure 7. Effect of pH for adsorption of Cr (VI) onto XTW

Effect of dose

Adsorption at constant temperature was carried out with different adsorbent dosages to optimize adsorbent dosage for removal of Cr (VI) from the aqueous solution. The adsorption efficiency of chromium uptake increases up to a certain level then it remains constant with increasing dosage of adsorbent varied from 10 mg to 100 mg at fixed pH, temperature, and adsorbate concentration as shown in Figure. Initially, the number of active sites of adsorbent is less at low dosages to uptake the chromium ion and as the number of adsorbent dosages increases then the percentage of re-model also increases with the increase of active sites. The removal percentage increases up to 25 mg adsorbent dose then the removal remains constant as the increase of adsorbent dose. Hence, the highest adsorption for 50 ppm adsorbate of hexavalent chromium is found to be 25mg adsorbent. There is no chance of adsorption when most of the adsorbate molecules occupy the active sites of the adsorbent, no matter how large the dosage of the adsorbent is.

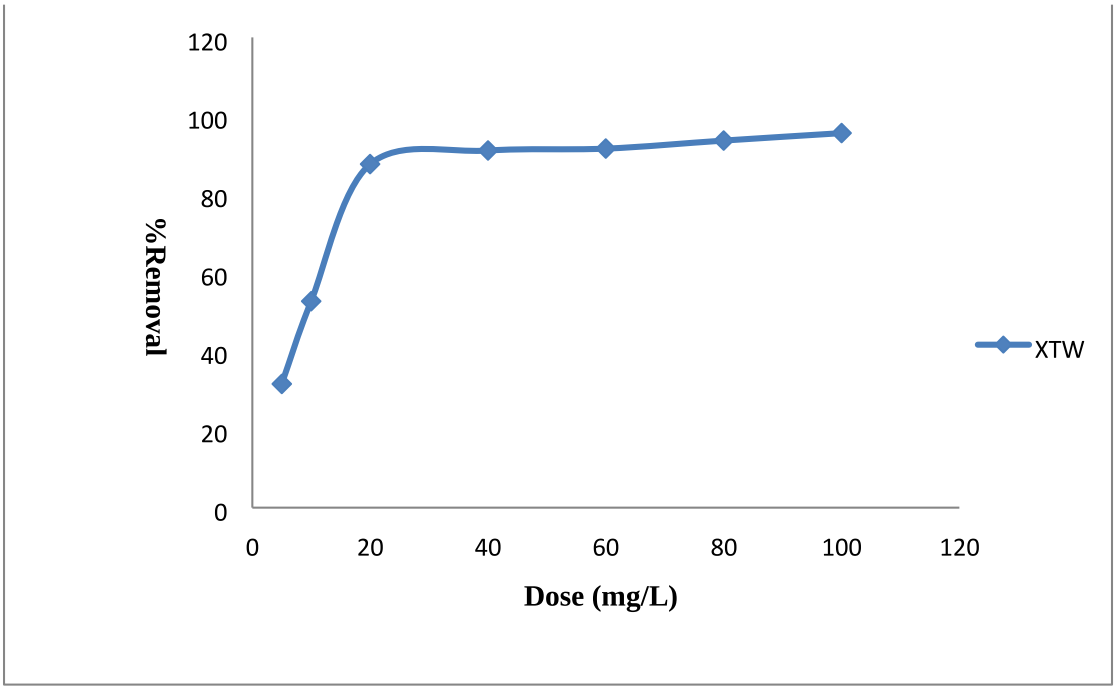

Figure 8. Effect of dose for adsorption of Cr (VI) onto XTW

Effect of Concentration

Adsorption of the metal ion increases with the increase in the equilibrium concentration of chromium ions. Eventually, adsorption is limited by the fixed number of active sites of the adsorbent and a plateau of isotherms is obtained. This is because, at low concentrations of chromium ions the active site of adsorbent is sufficiently available but at high concentrations, the active sites become fewer as compared to the chromium ions. Hence at high chromium concentrations, the adsorption amount becomes independent of the initial concentration of chromium ions. The figure below shows the Langmuir plot for the adsorption of hexavalent chromium onto XTW. The high value of the Langmuir correlation coefficient confirmed that the Langmuir model is best fitted.

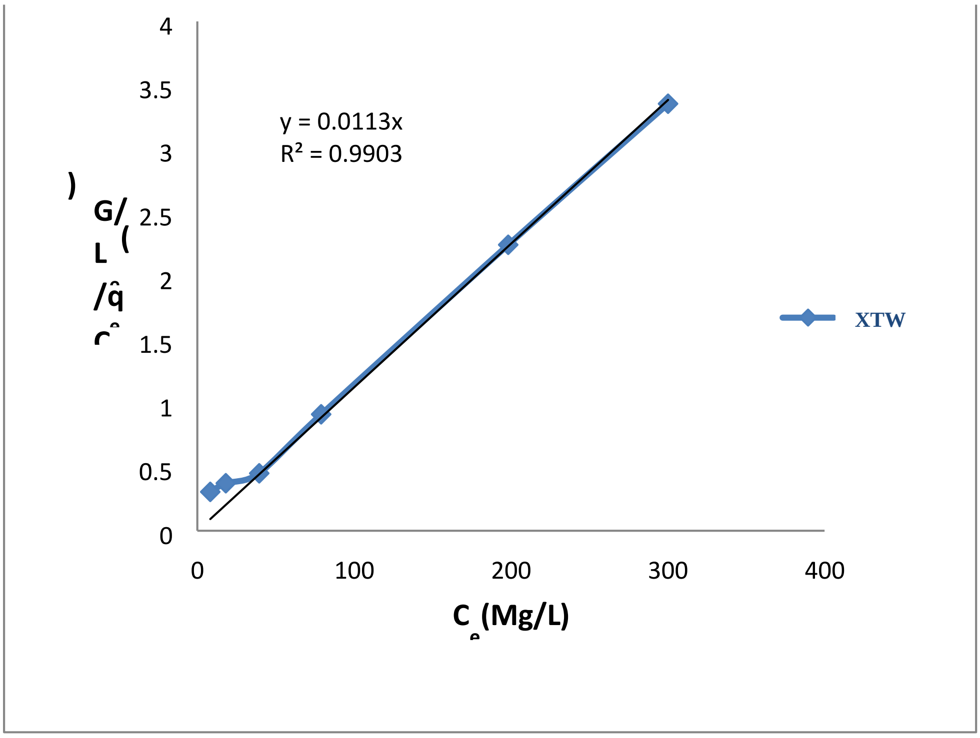

Figure 9. Langmuir isotherm plot for Cr (VI) onto XTW

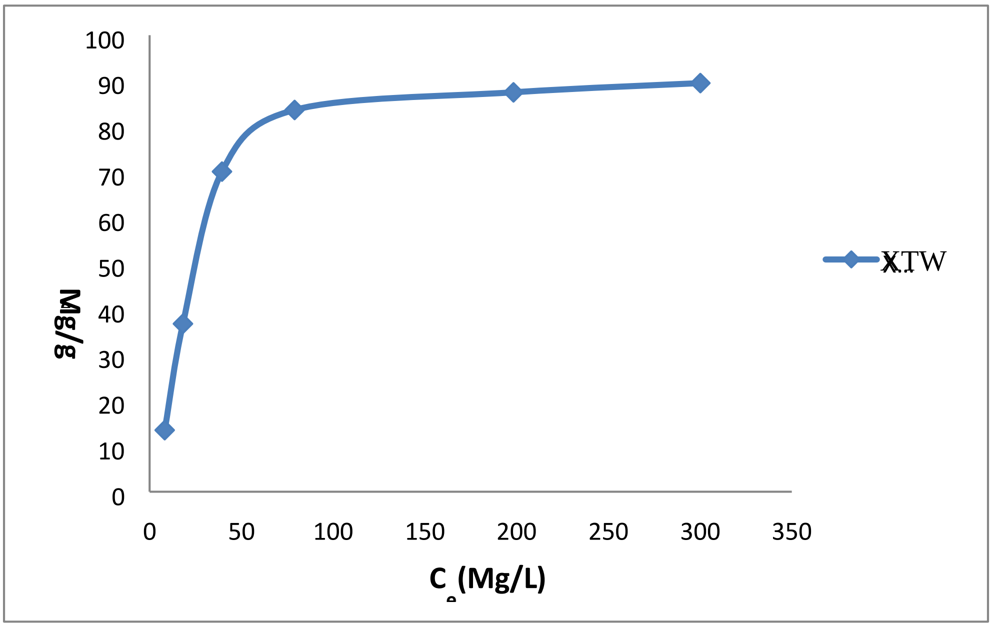

Figure 10. Effect of concentration on adsorption of Cr (VI) onto XTW

Effect of contact time

Figure below represents the sorption kinetics of hexavalent chromium onto XTW as the function of time at an initial concentration of 50 mg/L solution. The concentration of metal ions was analyzed at optimum pH 2.0 at different intervals of time by UV-Visible Spectrophotometer.

Initially, metal ions were rapidly adsorbed with increasing time and subsequently it became slow until the steady condition was attained. The optimum time for adsorption of hexavalent chromium using XTW as bio adsorbent was found to be 180 min.

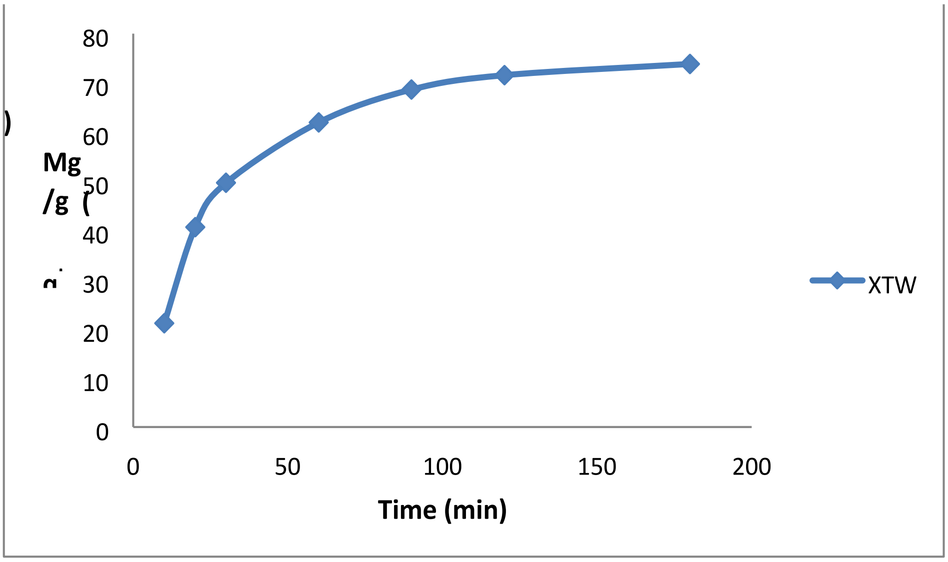

Figure 11. Adsorption kinetics of Cr (VI) onto XTW

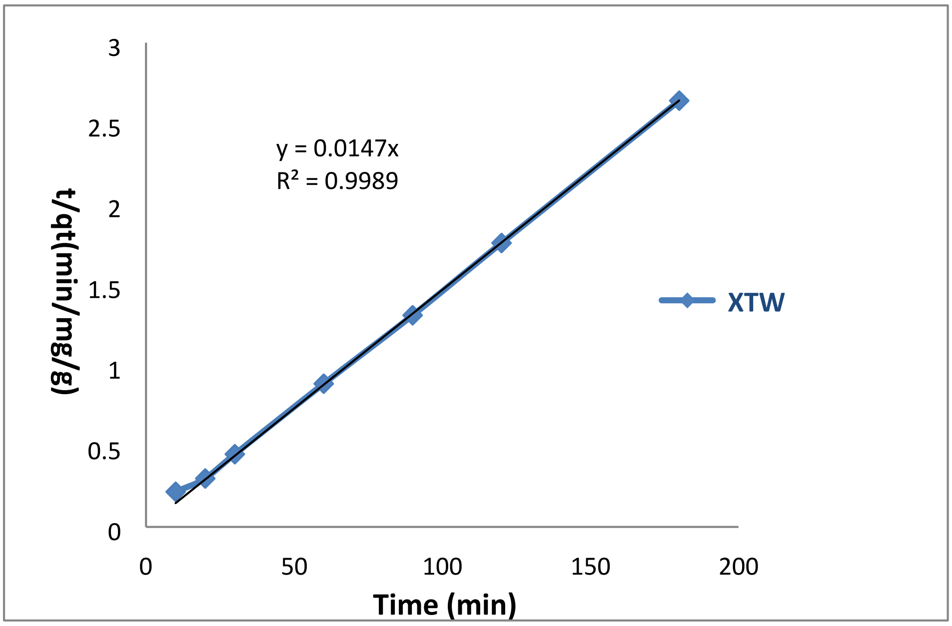

Figure 12. Pseudo second-order kinetic model for adsorption of Cr(VI) onto XTW

Discharged heavy metals with wastewater cause many environmental and health effects. The solution would be preventing the discharge of heavy metals directly into the water bodies. The adsorption experiments done in our research laboratory indicated that for adsorbent XTW is among the few good adsorbents which were previously researched. Thus it is concluded that XTW is a good adsorbent for the removal of Cr (VI).

- Xanthated tea waste was successfully prepared.
- The optimum pH was found to be 2.0 for XTW and the percentage adsorption was found to be 82.29%.
- Adsorption only increased from 20 min and the percentage adsorption at that time was 40.66% and 71.57% respectively.
- Percentage adsorption increased with ease in the adsorbent dose and found d to be optimum at 100mg (95.57%).
- The data best fitted for the Langmuir isotherm and pseudo-second-order kinetics.
- Finally, it was concluded that Cr (VI) can be removed from cost-effective, locally available, adsorbent which saves the environment as well as living beings from the harmful effects of Cr (VI).

Novelty and National Prosperity aspect of Project work

Heavy metal pollution is increasing day by day in the world. Different industries and power plants are producing a high level of different heavy metals along with chromium in the environment through effluents produced by them. These heavy metals are very harmful to living beings and the environment. Chromium in its hexavalent form is a major toxic pollutant that entered the water stream through various industrial operations. The source of chromium contamination includes the disposal of chromium-containing waste from different industries in water sources without any treatment. To control chromium pollution industries should discharge their waste only after proper treatment. For the treatment of industrial wastewater adsorption is the most effective method and we prepared a bio adsorbent from tea waste.

This method has many advantages over other techniques such as low operating cost as this method. It does not require a large initial investment, reusability of biomaterial, selectivity for specific metal, short operation time, etc. Furthermore, biological materials are frequently available from agriculture and animal waste. From the results of the project work, it can be concluded that tea waste can be used as a very good bio-adsorbent. With the simple modification of freely available tea waste, we can treat the wastewater released from industries and can make the environment neat and clean around us. This can also help to improve the health of animals and human beings.

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