PREPARATION OF CHEMICALLY MODIFIED MIXED FRUIT PEELS WASTE ADSORBENT FOR REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION

BY: KEBEDE MAMO

A THESIS SUBMITTED TO THE DEPARTMENT OF APPLIED CHEMISTERY

PRESENTED FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN APPLIED CHEMISTRY (INDUSTRIAL CHEMISTRY)

SCHOOL OF APPLIED NATURAL SCIENCE

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Approval Sheet

BY

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As thesis advisor, we hereby certify that we have read and evaluated this thesis paper under our guidance, by Kebede Mamo entitled: **"Preparation of Chemically Modified Mixed Fruit Peels Waste Adsorbent for Removal of Chromium (VI) from Aqueous Solution "** and submitted in partial fulfillment of the requirement for degree of Master of Science in Chemistry, the Graduate program of the department of Chemistry and has been carried out by Kebede Mamo ID № GSR /0163/09, under our supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

Major advisor	Signature	Date
Co-advisor	Signature	Date

As members of the board of examiners for the M.Sc. thesis open defense examination, we certify that we have read and evaluated the thesis paper prepared by Kebede Mamo and examined the candidate. We recommended the thesis paper to be accepted as fulfillment for the requirements of the thesis guideline of Adama Science and Technology University/Applied Chemistry program.

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Department Head	Signature	Date
School Dean	Signature	Date

DECLARATION

I hereby declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Name: Kebede Mamo

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This M.Sc. thesis has been submitted for examination with our approval as thesis advisor

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
BET	Brunauet Emmett – Teller
BOD	Biological Oxygen Demand
CMBO	Chemically Modified Banana and Orange
CMBOT	Chemically Modified Banana, Orange and Turmeric
COD	Chemical Oxygen Demand
CPAC	Commercially Prepared Activated Carbon
DPC	Dipneyle Carbazide
EDX	Energy Dispersive X- ray Spectroscopy
FP	Fruit Peel
FPW	Fruit Peel Waste
FT-IR	Fourier Transform Infrared Spectroscopy
RBO	Raw Banana and Orange
RBOT	Raw Banana ,Orange and Turmeric
RPM	Revolution Per Minute
SEM	Scanning Electron Microscopy
UV-Vis	Ultra Violet Visible Spectroscopy
WHO	World Health Organization

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ABSTRACT

Hexavalent chromium, (VI) from industrial effluent is a major water pollutant whose concentration needs to be reduced with in permissible limits. Therefore, in this study the modified mixed fruit peels (banana and orange peels) biomass with and without turmeric was investigated as an adsorbent for Cr(VI) removal from aqueous solutions. The adsorbents were prepared from banana, orange and turmeric after drying in an oven for 2hr at 80 ^oC and powdered to pass a micro sieve (250μm).The powdered fruit waste was mixed in equal proportion to yield mixed banana and orange (RBO) and mixed banana, orange, and turmeric(RBOT). A portion of this mixed powder was chemically modified by using H_3PO_4 to yield chemically modified mix of banana and orange (CMBO), and chemically modified mix of banana, orange and turmeric (CMBOT). Batch adsorption method was used to evaluate efficiency of adsorbent by varing the different parameters such as pH (1-5), adsorbent dose (0.2g – 2.5g), initial concentration of adsorbate (20mg/L - 80mg/L), and contact time (30min - 120 min) at room temperature.The concentration of Cr(VI) were measured using an ultraviolet-visible (UV-Vis) spectrophotometry using 1,5diphenylcarbazide at 540nm. Adsorbents were characterized using spectroscopic techniques including FT-IR and SEM-EDX to know the functional group of the adsorbents, pore properties and composition respectively. SEM Imaging indicated that the chemical modification increased the adsorption site of the adsorbents. The optimum parameters pH=2, adsorbent dose of 0.5 g , initial concentration of 60 (mg/L) and contact time of 60 min for CMBOT,RBO,RBOT and 60min of CMBO,were obtained. The maximum adsorption of CMBOT, CMBO, RBO and RBOT were found to be 5.99, 5.99, 5.79, 5.78 mg/g, respectively. The results showed maximum removal of Cr(VI) 99.83%, 99.75%, 96.5%, and 96.33% for CMBOT, CMBO, RBO, and RBOT, respectively. The experimental data were best fitted the Freundlich adsorption isotherm model (r^2 = 0.960, 0.780, and 0.285) for CMBOT, RBOT, and RBO respectively while CMBO best fit to Langmuir (r^2 =818). Moreover, the result showed pseudo second order fit experimental result and this reveals that the adsorption is physical. In general, the observed result confirmed Cr(VI) removal efficiency of fruit peels were enhanced by mixing fruit peel biomass and subsequent chemical modification , so that it can be used effectively and sustainably in waste water treatments technology. Moreover, the sludge of mixed fruit peel formed is biodegradable and environmentally friendly and therefore attractive in hexavalent chromium removal in water.

Keywords: Adsorption, Chromium, Adsorption thermodynamics, Mixed fruit peel, and Chemical modification

1. INTRODUCTION

1.1 Background

Pollution of water with heavy metals emanated from different sources is considered as a serious environmental issue. These metals are not biodegradable and can be accumulated in living tissues**,** causing various diseases and disorders [1]. For instance, Wastewater containing a significant quantity of chromium is discharged from the different industrial sector such as tanneries, electroplating, paint and pigments, mining, textile dyeing, cement, paper, power plants, and steel manufacturing, fertilizers and photography industries [2].

The presence of chromium even in trace amount in river water and other reservoir can have toxic influence on aquatic life. Chromium enters into water body in the form of two oxidation state as Cr (III) and Cr (VI) which are stable in the aqueous solution. However, Cr (VI) is 100 -1000 times more toxic to organisms than Cr(III) and more readily transported in water and soils [3].

The toxicological impact of chromium (VI) originates from its oxidizing ability as well as from the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the animal cell. Since Cr (VI) has carcinogenic, mutagenic and teratogenic properties, discharge from such industries has the potential to contaminate water bodies. As result of the health problems associated with chromium pollution in water, there are several methods conventionally used to remove chromium from industrial effluents. The conventional methods used include chemical precipitation, coagulation, flotation, ion - exchange, reverse osmosis, electrochemical treatments, cementation, membrane separation, hyper filtration, evaporation, oxidation, and solvent extraction methods [4]. However, these processes have significant disadvantages such as incomplete metal removal, high reagent cost and energy requirements, and generation of toxic sludge or other waste products that require disposal and, especially at low level of chromium concentration 1-100 mg/L [5].

On the other hand, adsorption is by far most versatile and effective method for removing any contaminants like heavy metal, especially, if combined with appropriate regeneration steps. This solves the problem of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used [6]. In the last few years, several approaches have been reported to utilizing inexpensive and effective adsorbent for removal of Cr(VI) from aqueous solutions [7].

The removal efficiencies of the various non-conventional adsorbents towards adsorbate removal vary generally between 50% and 90% depending on the characteristics of effluent such as chromium content, chloride, sulfide, COD and BOD, pH and particle size of the adsorbent etc. Hence, low-cost adsorbents

can be employed efficiently in removal of heavy metals. The use of non-conventional adsorbents such as banana, potatoes and orange peel waste are much cheaper relative to conventional adsorbents, specifically when adsorbents were locally available. Moreover this non-conventional adsorbents require simple alkali/and or acid treatment for the removal of lignin before application in order to increase their efficiency and require less maintenance and supervision [8].This adsorption is now reorganized as an alternative technology for the chromium removal due to local availability, large surface area, technical efficiency, and cost effectiveness.

Despite of the maximum adsorption capacity of the different adsorbents used to remove chromium such as potato peels [9], orange peel [10], and powdered activated carbon [11]; adsorbents like powdered activated carbon has problem of reusability and higher production cost [12]. Moreover, the problem of the management of fruit peels to get individual fruit peel causes considerable concern to the fruit peel users, thus implying the need to identify a means these fruit peels are effectively used without segregation to enhance adsorption capacity of chromium from waste water. Because most of these fruit peel are effective at low Cr(VI) concentrations and reduce cost.

Banana and Orange are among the locally available agricultural by-products in Ethiopia. They are mostly composed of lignin, hemicelluloses, proteins, lipids and cellulose, as well as other polar functional group-containing compounds, which include alcohols, aldehydes, ketenes, hydroxyl, ester, amino, carboxyl, carbonyl, and phosphor group, carboxylates phenols and ethers possibly used as chromium binding site [13]. These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution [14].However, application of these raw plant materials as adsorbents is limited due to leaching of organic compounds such as cellulose, lignin, pectin and lignocelluloses into solution according to Yenench, *et.al* [15]. Therefore, in this research the adsorption capacity of these waste peels were improved for the removal of Cr(VI) from aqueous solution through chemical modification.

1.2. Statement of the Problem

Chromium has been considered as top 16th toxic pollutant, teratogenic and carcinogenic characteristic to human health. The two most stable oxidation states of chromium which persist in the environment are Cr (III) and Cr (VI).They have contrasting toxicities, mobilities and bioavailabilities, in which Cr(III) is important in human nutrition (especially in glucose metabolism), Whereas, most of the hexavalent compounds are toxic, several can even cause lung cancer. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [16]. In Ethiopia, due to increasing number of industries which could be source of effluents containing chromium, the problem of contamination of water is unavoidable. Even though different reports are available on chromium removal using different natural adsorbent; removal of chromium from aqueous solution using mixed fruit peel waste has not been yet studied in Ethiopia.

In addition in developed countries, toxic heavy elements discharged from different industrial areas along with polluted liquid waste; have been successfully removed by high resolution and costly treatment methods. However, in developing countries, like Ethiopia, such advanced treatment methods are not widely used due to their high cost, feasibility and economic disadvantage. Moreover the the methods are difficult to operate, and also the processes involve use of chemicals and synthetic polymers whose impact on the environment has not been entirely studied. Therefore, it is an urgent need to develop cost effective, locally available and efficient treatment technologies, preferably using low cost adsorbent techniques for effective removal of (VI) from aqueous solution. In this regard to this study focused on investigating the potential of locally available fruit peels for effective removal of Cr(VI) from aqueous solution.

1.3. Objectives of the Study

1.3.1. General Objective

The general objective of this study was to prepare chemically modified, characterize, and evaluate the potential of mixed fruit waste peels as adsorbent materials for chromium removal from aqueous solution.

1.3.2. Specific Objectives

The specific objectives of the study include:

- To preparation of fruit waste peels powder and chemical modification for the removal of chromium from aqueous solution.
- Characterization of both unmodified and chemically modified adsorbents prepared from mixing banana and orange peels with and without turmeric peel
- Optimize the removal efficiency of chromium from aqueous solution by varying pH, Initial concentration of adsorbate, adsorbent dosage and contact time
- To study the adsorption isotherm and kinetics

1.4. Significance of the Study

Most conventional technologies for the removal of Cr(VI) from aqueous solution suffer from certain drawbacks such as high capital and/or operational costs. Therefore, there is a need to develop comparably efficient, low cost economically viable process technologies from easily available materials, which can adsorb Cr(VI). To develop such a process, it is at the same time very important to know the level of chromium in water bodies and around different industries especially leather industry since high level of chromium can cause carcinogenic and teratogenic characteristics on human health. The present study will aprovide information regarding the removal efficiency of mixed fruit peel waste from aqueous solution. Further studies can also be conducted based on this study.

1.5. Scope of the Study

The study was limited to adsorption of chromium (VI) from aqueous solution on mixed fruit waste peels adsorbent using different adsorption methods. Mixed fruit peels which are used for the removal chromium of are used as reducing agents. The characterization of the prepared adsorbents limited to FTIR (functional group analysis), UV-Vis (total chromium analysis in aqueous solution) and SEM-EDX (absorbent morphology and elemental composition analysis).

2. LITRATURE REVIEW

2.1. Water pollution

Water pollution is a major problem in the global context. Water used in many industries creates a wastewater that has a potential hazard for our environment because of introducing various contaminants such as heavy metals into soil and water resources. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment [17]. Heavy metals are an important category of pollutants and as such have major detrimental impacts on both human health and the health of terrestrial and aquatic communities and ecosystems. A number of metals have been included in the term "heavy metal" [18].The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration because not degrade in to harmless end products,. "Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water. However, being a heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements.

Heavy metals differ widely in their chemical properties, and are used extensively in electronics, machines and the artifacts of everyday life, as well as in high-tech applications. As a result they are able to enter into the aquatic and food chains of humans and animals from a variety of anthropogenic sources as well as from the natural geochemical weathering of soil and rocks. The main sources of contamination include metal plating industries, mining activities, battery manufacture, tanneries, petroleum refining, paint manufacture, pigment manufacture, printing and photographic industries [19]. Other sources are wood processing industry where a chromate copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium. According to the world health organization (WHO, [20] the permissible limit of Cr (VI) is 0.05 mg/L for drinking water and 0.1 mg/L for discharge to inland surface water.

With increasing generation of metals from technologies activities, the problem of waste disposal has become one of paramount importance. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans. The problems are exacerbated because metals have a tendency to be transported with sediments, are persistent in the environment and can bio accumulate in the food chain [21].

2.2. Speciation and Toxicity of Chromium

Chromium is a heavy metal, and it is the 16th most abundant element in the earth's crust. It may occur in nine different forms of oxidation state ranging from Cr (-II) up to Cr (+VI), but the two common valence states are trivalent Cr (III), the most stable, and hexavalent Cr (VI) which is not thermodynamically stable. The conversion of Cr (VI) to Cr (III) occurs readily by a variety of reducing agents in water and soil, but a few oxidants in natural water can oxidize Cr (III) to Cr (VI). Solubility of chromium (III) depends on pH; decreases dramatically at pH value greater than 4.5 and Cr(III) can form stable complexes with organic legends at pH value as high as 8.5 [22]. Both trivalent and hexavalent chromium have different forms in wastewater depending on different conditions. Inorganic chromium (III) may exist in aqueous solution as hydroxo species, $Cr(OH)^{2+}$, $Cr(OH)_3$, $Cr(OH)_4^-$, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$,and a mixed ligand complexes, such as $Cr(OH)Cl^+$, $Cr(SO4)^+$. However $(OH)^{2+}$predominate at pH 5. Whereas, Chromium (VI) may be present in aqueous solutions mainly as chromate, dichromate, hydrogen chromate, chromic acid, and hydrogen dichromate. The last two species have been detected only in strongly acidic solutions. In typical surface waters when concentration of chromium is less than 5 μg/L only $HCrO_4^-$ and CrO_4^{2-} can be found [23].

In the environment, trivalent chromium Cr(III) is generally harmless due to its weak membrane permeability. Hexavalent chromium Cr (VI), on the other hand, is more active in penetrating the cell membrane through passages for iselectric and isostructural anions such as SO_4^{2-} and HPO_4^{2-} channels and these chromates are taken up through phagocytosis. Cr(VI) is a strong oxidizing agent and can be reduced to give ephemeral species of pentavalent and tetravalent chromium that are different from that of Cr(III). Stabilization of the pentavelent form is carried out by glutathione and hence intracellular reduction of Cr(VI) is considered a detoxification mechanism when reduction occurs away from the target region. However if intracellular reduction of Cr (VI) occurs near the target site, it may serve to activate Cr. The reactions between Cr(VI) and biological reductants like thiols and ascorbate result in the production of reactive oxygen species such as superoxide ion, hydrogen peroxide, and hydroxyl radical, ultimately leading to oxidative stress in the cell causing damage to DNA and proteins [24]. Cr (VI) also more mobile than Cr (III) and it can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged. Interestingly enough, irritation of the skin a most frequently reported human health effect from exposure to Cr (VI) taking the form of skin ulceration (dermatosis) and allergic sensitization (dermatitis) [25]. Indeed, dermatosis was the first observed health effect associated with chromium (VI) exposure, although improved industrial hygiene practices have greatly reduced its incidence. Allergic contact dermatitis is the most prominent reaction

from the interaction of chromium with skin. According to literature surveys, Cr(VI) has been found to be much more dangerous than Cr(III), since Cr(VI) enters the cells more readily than does Cr(III) and is eventually reduced to Cr(III). Because of its mutagenic properties, Cr(VI) is categorized as a group one human carcinogen by the International Agency for the Research on Cancer [26].

2.3. Methods of Chromium Removing Technologies from Waste Water

Chromium contamination is common all over the world. Continuous discharge of industrial, domestic and agricultural wastes in rivers and Lakes causes deposit of pollutants in sediments. Such pollutants contain chromium, which endanger public health after being incorporated in food chain. Excessive amounts chromium ions can be toxic for organism through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Several methods have been used for the treatment and removal of chromium ions. The commonly used procedures include chemical precipitation, coagulation, electrodalysis, ion exchange, reverse osmosis, adsorption, and solvent extraction [27].

2.3.1. Ion Exchange

Ion exchange is a reversible chemical reaction method used successfully in the industry for the removal of heavy metals from effluent. It is physical process in which an ion with a high affinity for the resin material of the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. As water flows through, dissolved Cr (VI) ions bind to the resin and displace the previously bound ions (usually Cl^- or OH^- ions). The resins used for Cr sequestration are typically either a naturally occurring inorganic zeolite or a synthetic weak base or strong base anion exchanger resin. Once the resins have accumulated Cr on enough exchange sites that breakthrough surpasses a threshold value, they must be regenerated. Ion exchange resins are capable of reducing Cr (VI) concentrations to less than the detection limit. Resins are typically most effective at low pH values, because Cr (VI) will be present as $HCrO_4^-$ and $Cr_2O_7^{2-}$, not as CrO_4^{2-}. The ratio of ion exchange sites to Cr ions sequestered is then 1/1. When CrO_4^{2-} is present, two ion exchange sites are used to sequester each Cr ion. Competition by other anions (namely SO_4^{2-}, nitrate (NO_3^-), and Cl^-) is not a problem in most applications, since Cr has a higher affinity for all polymeric anion exchangers. The disadvantage of this method is highly sensitive to the pH of the solution and corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced [28].

2.3.2. Electro Dialysis

Electro dialysis (ED) is a membrane separation process in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics [29]. In the electro dialysis process, ionic components of a solution are separated through the use of semi permeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the Electro dialysis process for wastewater renovation include chemical precipitation of Salts with low solubility on the membrane surface.

2.3.3. Chemical Precipitation

Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation [30].

$$M^{2+} + 2(OH^{-}) \longrightarrow M(OH)(s) \quad \ldots\ldots 1$$

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. Precipitation of Cr (III) occurs as $Cr(OH)_3(s)$, $FeCr_2O_4(s)$, or $Fe_xCr_y(OH)_3(s)$ [31]. As pH increases, OH^- concentration increases and more Cr precipitate. Organics can complex with dissolved Cr, making removal by precipitation or adsorption difficult. The precipitation of Cr (III) is useful for increasing Cr (VI) to Cr (III) reaction rates, by Le Chatelier‟s principle. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, toxic compounds and the long-term environmental impacts of sludge disposal [32].The chemical reactions of a typical chrome recovery process are:

$$Cr_2(SO4)_3 + 3MgO + 3H_2O \longrightarrow 2Cr(OH)_3 + 3MgSO_4 \quad \ldots\ldots 2$$

$$2Cr(OH)_3 + 3H_2SO_4 \longrightarrow Cr_2(SO4)_3 + 6H_2O \quad \ldots\ldots 3$$

2.3.4. Coagulation - Flocculation

Coagulation-flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation [33].In spite of its advantages; coagulation-flocculation has limitations such as high operational cost due to chemical consumption. To overcome such problems, electro-coagulation may be a better alternative

than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge [34].

2.3.5. Adsorption Study

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a Solid or liquid (adsorbent), forming a molecular or atomic film (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is an operative in most physical, biological, and chemical systems and widely used in industry. At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed [35].

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bind with whatever happens to be available. The exact nature of the binding depends on the details of the species involved, but the adsorbed material is generally classified as exhibit physisorption or chemisorptions [36].

The sorption mechanism of hexavalent chromium can be described by four different ways which are: 1) anionic sorption, 2) sorption-coupled reduction, 3) anionic and cationic sorption and 4) reduction and anionic sorption. In Anionic sorption, negatively charged Cr species CrO_4^{2-} and $Cr_2O_7^{2-}$ bind to positively charged functional groups on the surface of sorbents. Electrostatic attraction and/or surface complexation provide the binding phenomenon between the opposite charges. In the anionic sorption mechanism, the sorption of Cr(VI) is increased at low pH whereas at high pH Cr(VI) sorption decreases. At low pH functional groups of the sorbent become protonated, and easily attract negatively charged chromate ions. On the other hand, at high pH deprotonation takes place because functional groups of the sorbent become negatively charged and do not attract negatively charged chromium compounds [37].

Sorption-coupled reduction is the mechanism that deals with the reduction of Cr(VI) to Cr(III) using a sorbent in an acidic medium [38]. Then the resultant Cr(III) is sorbed from the solution. In the anionic and cationic sorption mechanism, part of the Cr(VI) is reduced to Cr(III), and then both the Cr species are sorbed to the surface of the sorbent. According to the reduction and anionic sorption mechanism, a part of the Cr(VI) is reduced to Cr(III); afterward Cr(VI) is mainly sorbed by the sorbent while Cr(III) remains in the solution [39]. Fruit waste peels (FP) has been considered as a potential adsorbent for the adsorption of (IV) from aqueous solution and waste water.

2.4. Property and Application of Fruit Peels Waste

The surface properties of fruit peel (FP) indicate that it has more acidic sites and different functional groups with rough and porous surface. This blend of properties makes it suitable as an adsorbent. Heavy metals, dyes and organic pollutants can be successfully removed from aqueous solution using FP, as heavy metals show higher affinity toward FP. For these reasons, there is an urgent need to seek resource and value-added use for fruit wastes. In fact, inexpensive and readily available use of agri-food industry waste is highly cost-effective and minimizes environmental impact. One of the most beneficial approaches is to recover the bioactive constituents, especially the phenolic compounds, making full use of them in the food, industrial, pharmaceutical as well as cosmetics industry [40]. Thus, utilization of the fruit wastes as sources of bioactive compounds may be of considerable economic benefits and has become increasingly attractive in the recent time.

Yet, in recent studies, the antioxidant potency and the content of phenolic compounds found to be high in the peel and seed of some fruits [41], including that residues have the potential to be utilized as a resource of bioactive compounds , such as natural anti oxidants. The antioxidant property of the plant material is due to the presence of many active phytochemicals including vitamins, flavonoids, terpenoids, carotenoids, cumarins, lignin, saponin, plant sterol …etc. Because of the functional group present , they have a chelating activity, antioxidant/radical scavenging capacity and reducing power ability of the produced extracts were investigated [41].

Swarnabala Jena and Rajesh Kumar Sahoo [42] reported on removal of Pb (II) from aqueous solution using fruits peel as a low cost adsorbent. Adsorption of Pb(II) ions onto four different fruits peel i.e. orange, lemon, banana, watermelon were investigated with the variation in the parameters of pH 2 except banana peel which was at pH 4 , contact time 40 min , initial metal ion concentration 10 mg/L, adsorbent dose 0.2 g / 50 mL, agitation speed 150 rpm and at room temperature . Batch adsorption studies indicated maximum of 91%, 94%, 92%, 96% adsorption capacity for orange, lemon, banana, and watermelon respectively. SEM study gives a detailed morphology of the fruits peel. FTIR study of adsorbents at the optimized condition was carried out using JASCO-410 model IR spectrometer to identify the different functional groups that are responsible for the adsorption. The important functional groups like hydroxyl, alkenes, aromatic nitro, carboxyl ate anion, ester, silicon oxide, sulphonic acid etc. present in the fruits peel were responsible for the chemical adsorption. Langmuir adsorption model was best fit and the process is endothermic showing monolayer adsorption.

2.4.1. Properties and Application of Turmeric Peel

Turmeric powder is approximately 60 -70% carbohydrates, 6-13% water, 6-8% protein, 5-10% fat, 3-7% dietary minerals, 3-7% essential oil 2-7% dietary fiber, and 1-6% curcuminoids [43]. Phytochemical components of turmeric include diarylheptanoids, which occur from numerous curcuminoids, such as curcumin and demethoxycurcumin. Curcuma plants have a camphoraceous aroma and contain many functional compounds such as volatile oils, terpenes, phenolics and flavonoids, which are strong antioxidants. Phenolics and flavonoids possess pharmacological activity (ant carcinogenic, anti-inflammatory properties) due to their radical scavenging activity and lipid antiperoxidation effects [44]. Since free radicals are the cause for several major disorders, evaluation of antioxidant compounds/ activity in plants could result in the discovery of natural antioxidants with pharmacological and food value. Curcumin can bind with heavy metals such as cadmium, lead and chromium, thereby reducing the toxicity of these heavy metals.

Figure 1**.** The turmeric root peel and its structure (source Mizan Tepi agriculture institute)

2.4.2. Properties and Application of Banana Peel

Banana *(Musa sp. family Musaceae*) develops in hanging clusters, with nearly 20 fruits/hand (tier) and 3-20 hands in each cluster. The average fruit weight is about 125 g with nearly 25% dry matter and 75% water. Banana peel (BP) comprises about 30 - 40% (w/w) of fresh banana. The composition of ripe BP is as follows: crude protein (8%), ether extract (6.2%), soluble sugars (13.8%) and total phenolic compounds (4.8%). The main components of BP are cellulose, hemicellulose, chlorophyll, pectin and other low-molecular weight compounds [45].

KKIU Aruna Kumara *et al.* [46] revealed by laboratory investigations, banana peel contains pectin (10-21%, Lignin (6-12%),cellulose (7.6-9.6%) and hemicelluloses (6.4-9.4 %) and also investigated that banana peel is capable of absorbing 5.71, 2.55, 2.800, 6.88, 7.97 and 5.80 mg/g of Ca^{2+},CO^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} respectively from aqueous solution. Banana peels also rich in dietary fiber, proteins, essential amino acids, polyunsaturated fatty acids and potassium. Absorption capacity is however

dependent upon several factors including solution pH, dose of absorbent, metal concentration, contact time and shaking speed.

Renata *et al.* [47] studied solid phase extraction of copper and lead from river water using minced banana peel above pH 3.The medium was characterized by FTIR which showed absorption bonds of carboxylic and amino groups at 1730 and 889 cm-1 respectively. The absorption isotherm fitted by Langmuir model showed maximum absorption capacities of 0.33 and 0.20 mol/g for Cu (II) and Pb(II) respectively.

Rafique *et al.* [48] obtained the adsorption efficiency of 88% on peels of banana, lemon, and peels composite (in the BP:LP ratio of 1:1) as possible adsorbents for the purification of industrial effluents polluted with heavy metals like Pb, Cd, Ni, and Cu.

Ali *et al*. [49] Study on removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent at pH 3, initial adsorbate concentration 400 mg/L, Dosage 4 g/L and contact time 120min. The surface morphology of adsorbent was characterized by scanning electron microscopy (SEM) before and after the adsorption. The removal efficiency was 96% and the adsorption data were fully fitted with the Freundlich and Langmuir isotherm model and followed a pseudo-second order kinetic model.

Mandeep Kumar and CB Majumder [50] study on biological removal of chromium (VI) from synthetic waste water by using Hydrochloric acid treated banana peel at pH 2 , initial chromium concentration 100 mg/L, dosage 2g/L and contact time 60 min. The maximum removal efficiency was 99 % and the data was best fitted Pseudo second order model and the equilibrium isotherm data were comparing by using the Langmuir, Freundlich and Temkin isotherm models in which Freundlich isotherm was found to be fitted best

Ricardo Díaz Martín *et al.* [51] reported on kinetic study of absorption of chromium (VI) using canary bananas peels in contaminated water. The maximum removal efficiency was 96% at pH 2 , initial chromium concentration 50 mg/L , dose 0.5g/100mL , contact time 30 min an and agitation speed of 120 rpm. The adsorption system obeyed Pseudo second order kinetics with R^2value of 0.999. The adsorption phenomenon demonstrated here was monolayer represented by Langmuir isotherm with R^2 alue of 0.99 and the Langmuir constants k and q_m was found to be 1,53 (L/mg) and 10,09 (mg/g).

Figure 2. Banana plant and its peel (source from Adama town market)

2.4. 3. Properties and Application of Orange Peel

Orange (*Citrus sinesis, family Rutaceae*) contains orange peel (OP) which is an important byproduct. OP comprises cellulose, hemicelluloses, lignin, pectin (galacturonic acid), potassium oxide (K_2O) with 1.72%, calcium oxide (CaO) with 1.31% ,

chlorophyll pigments and other low-molecular weight compounds (e.g. limonene). This component contain various functional groups ,such as hydroxyl and carboxyl group which make the orange peel a potential adsorbent for removing metal ion from aqueous solution. Traditionally, OP is treated to obtain volatile and nonvolatile fractions of essential oils and flavoring compounds. In addition, OP has been reported to have germicidal, antioxidant, and anti carcinogenic properties, and thus may be effective against breast and colon cancers, skin inflammation, muscle pain, stomach upset and ringworm [52].

Mohammad Ajmal *et al.* [53] studied the use of fruit peel of orange for removal and recovery of Ni (II) from electroplating waste water. They also studied the ability of fruit peel of orange to remove Zn, Ni, Cu, Pb and Cr from aqueous solution. The absorption was in the order Ni (II) > Cu(II) > Pb(II) > Zn(II) > Cr(III). The adsorption follows first order kinetics. The process is endothermic and follows Langumir and Freundlich isotherm. The absorbed Ni (II) can be recovered using 0.05 M HCl solution. However the recovery of Ni (II) by column operation is higher (95.8%) as compared to batch process (76%).The spent absorbent can be regenerated and reused making the absorption process more economical.

Nitin . M. Rane and R. S. Sapkal [54] reported on chromium (VI) removal by using orange peel powder in batch adsorption. A maximum of 98% removal efficiency was obtained at pH 1.25 initial chromium concentration 2 ppm , dosage 2g and contact time 6 min, agitation speed 180 rpm , particle mesh size 180 and temperature 30^{o}C The change in lattice structure of adsorbent before and after adsorption

was analyzed by FTIR and SEM analysis. The Freundlich and Langmuir isotherm were studied. The kinetics investigation follows pseudo second order behavior.

Shadreck Mandina *et al.* [55] work on the removal of chromium (VI) from aqueous solution using chemically modified orange (citrus cinensis) peel. The adsorbent was characterized by FT-IR spectroscopy and BET. The characterization of the orange peel biomass was suggested the possible contribution of carboxyl and hydroxyl groups in Cr (VI) adsorption. According to their study adsorbent was chemical modified using sodium hydroxide to enhanced adsorption capacity. The adsorption efficiency of the orange peel was pH 2 being optimal, equilibrium time 180 min, optimal adsorbent dosage at 4.0 mg/L. The increase in initial Cr (VI) ion concentration led to an increase in the percentage removal of Cr (VI). The maximum removal efficiency 29.8% and 29.6% for modified and raw orange peel respectively. The adsorption data fitted well with the Freundlich isotherm model with R^2 = 0.987 for the raw orange peel and R^2 = 0.995 for the modified orange peel. The Freundlich constants Kf and n were 97.07 [mg/g (L/mg)n] and 0.79 (g/L) for the raw orange peel and 139.0 [(mg/g)(L/mg)n] and 0.815 (g/L) for modified orange peel respectively.

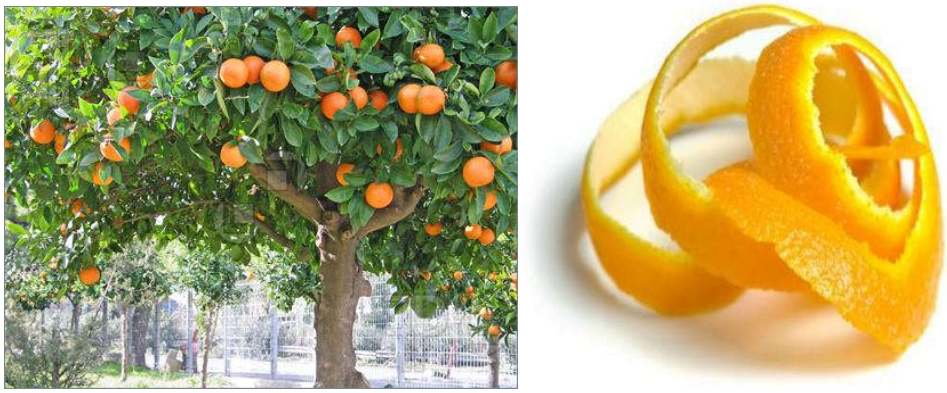


Figure 3. Orange fruit and its fruit peel (source from adama town market)

2.5. Characterization of adsorbent

2.5.1. Fourier Transform Infrared Spectrometry (FTIR)

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material when IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in

identification of every different kind of functional group. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present [56].

2.5.2. Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy (SEM-EDX)

The surface characteristics, structure and particle size distribution and elemental composition of adsorbent before and after adsorption characterized using scanning electron microscope (SEM-EDX). A scanning electron microscope (SEM) is a type of electron microscope that produces images of sample by scanning it with a focused beam of electrons. The morphological and topographical studies were carried out using electron microscope, which is a straight forward technique for the determination of morphology and size of solid catalysts [57]. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on the angle at which beam meets surface of specimen, i.e. on specimen topography. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created

2.6. Adsorption Mechanisms

It is a complex which involves several mechanisms that quantitatively and qualitatively differ according to the adsorbent types, its origin and its processing. Mechanisms involved in the adsorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro -precipitation, heavy metal hydroxide condensation onto the bio-surface, and surface adsorption [58]. The removal of anionic hexavalent chromium is a complicated process, in which reduction, surface complex formation, and ion exchange are involved. Hexavalent chromium can form surface complexes with the protonated functional groups on the adsorbents, such as -COOH, $-NH_2$, and $-SO_3H$. The Cr (VI) anions can also oxidize the secondary alcohol groups on the adsorbents, while being reduced to Cr (III) cations. The Cr(III) cations that formed from the redox reactions are then able to undergo ion exchange reactions with cationic alkaline metal ions such as Ca^{2+}, which are initially bound onto the adsorbents. Experimental evidences reported in the literatures have demonstrated that Cr(III) ions are accumulated onto seaweed biosorbents due to ion exchange. In addition, the carboxyl group can form metal complex due to coordination reactions [59].

Complexation: The metal removal from solution may also take place through complex formation on the adsorbent surface after interaction between the metal and active groups. Metal ions can bind to unidentate (single)ligands or to chelates.

2.7. Factor Affecting Adsorption Process

Effect of initial metal ion concentration: At low concentration the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions interact with the adsorbent and are removed quickly from the solution. However, the amount of metal ions adsorbed per unit weight of adsorbent, qe, is higher at high concentration [60]. This is probably due to the higher interaction between the metal ions and metal sequestering sites of the adsorbent.

Effect of Contact Time: The initial rapid rate of adsorption may be due to the availability of the vacant active surfaces of the adsorbents for anionic Cr(VI) species in the solution. The later slow adsorption rate could be due to the electrostatic hindrance caused by already adsorbed adsorbate species and the slow pore diffusion of the ions [3]. In general, the initial rate of adsorption is fast, and then a slower adsorption would follow as the available adsorption sites are slowly decreased. This is due to the fact that a large number of unoccupied surface sites are available for adsorption during the initial stage and after ascends of time the remaining unoccupied surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [61].

Effect of pH : More adsorption at acidic pH indicates that an increase in H^+ ions on the adsorbents surface results in electrostatic attraction between positively charged adsorbents surface and chromate ions because $HCrO_4^-$ is the dominant anionic form of Cr(VI) at lower pH [62]. In aqueous solution hydrolysis of $Cr_2O_7^{2-}$ takes place $Cr_2O_7^{2-} + H_2O \longleftrightarrow 2HCrO_4^-$ to from $HCrO_4^-$.Thus, although $Cr_2O_7^{2-}$ of $K_2Cr_2O_7$ was the source of Cr (VI) in the synthetic solution used in this study, at pH less than 6. The dominant ionic form of Cr(VI) at pH 2 is $HCrO_4^-$ while CrO_4^- is dominant in the range of pH > 7 based on the pKa values [63 - 64]. As the solution pH increases, CrO_4^{2-} and $Cr_2O_7^{2-}$ became prominent.

Effect of Adsorbent Dose: Adsorbent doses beyond the steady state do not improve adsorption due to availability of excess adsorption sites than that of sorbets [65]. Assuming that the number of adsorption sites per unit mass of adsorbents remains constant. At lower dosage of adsorbents, there are insufficient active sites that the adsorbate can easily occupy. However, at higher dosage, active sorption sites are sufficiently available for the adsorbate to occupy.

2.8. Adsorption Methods

2.8.1. Langmuir Adsorption Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. The model assumes maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The linear form of Langmuir isotherm model is described as [66].

$$\frac{Ce}{qe} = \frac{1}{KL\ qm} + \frac{Ce}{qm} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where Ce is the equilibrium concentration in liquid phase (mg/L), qe is the equilibrium amount of adsorbate (mg/g), qm is the maximum adsorption capacity (mg/g) and KL is the Langmuir constant (L/mg) related to the energy of adsorption.

2.8.2. Freundlich Adsorption Isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and is an indicator of the extent of heterogeneity of the adsorbent surface. . Its equation is given as;

$$qe = K_f Ce^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Where = freundlich constant, n = freundlich coefficient, the constant Kf is an approximate indicator of adsorption capacity and 1/n is a function of the strength of adsorption in the adsorption process. If 1/n = 1 then the partition between the two phases are independent of the concentration, If 1/n <1 normal adsorption and 1/n > 1 indicates cooperative adsorption [67].

The linear form of Freundlich isotherm is expressed as

$$\text{Log } qe = \text{Log } Kf + \frac{1}{n}\text{LogCe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

Where, qe represents the amount of adsorbed Cr (VI)per gram of adsorbent at the equilibrium (mg/g), Ce is the equilibrium solution concentration (mg/l), and K*f* and *n* are Freundlich constants, which represent adsorption capacity (mg/g) and adsorption intensity, respectively.

2.9. Kinetic Studies

In order to understand mechanism of adsorption and potential of rate controlling step, numbers of kinetics models have been used to determine experimental data of Cr (VI) adsorption

2.9.1. Pseudo - First Order Model

The pseudo-first-order kinetic model can be expressed linearly as [68].

$$\ln (qe - qt) = \ln qe - k1t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

Where qe and qt are the amounts of Cr (VI) ions adsorbed (mg/g) at equilibrium and at time t (min), respectively and K1 the rate constant of pseudo-first-order adsorption (min^{-1})

2.9.2. Pseudo - Second Order Model

The adsorption may also be described by pseudo-second order kinetic model if the adsorption does not follow the first order kinetics. Two assumption carried out by second order model first one is that rate limiting step is chemical adsorption and second one is process is second order.Pseudo- second order kinetics is the other type of adsorption kinetics that has been successfully applied to metal ions and organic substance. It state that the slowest step is chemical adsorption [69]. The linearzed form of its equation is expressed as;

$$\frac{dq}{dt} = k2(qe - qt) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 8$$

After integrating equation for boundary condition the equation becomes

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 9$$

Where = second order rate (g/mg min) and h = $K_2 qe^2$ is initial adsorption rate.

3. MATERIALS AND METHODS

3.1 Chemicals and Reagents

All chemicals were analytical grade and purchased from chemical shops in Addis Ababa. Standard buffer solution for pH meter calibration, HCl (37 %, Riedel-deHaën), Germany) , NaOH (sigma-Aldrich), H_3PO_4 (85% w/v Sigma-Aldrich), 1,5 diphenyl carbazide solution, Acetone (Sigma-Aldrich), H_2SO_4 (98 %, UNI-CHEM, Germany), potassium dichromate ($K_2Cr_2O_7$ 99.9 %, FINKEM, England) and Double ionized water for all preparation and purification.

3.2. Apparatus and Equipments

The materials and equipments for this study was: UV-Vis spectrophotometer (T 80 + - PG Instrument Ltd), Fourier Transform Infra-red Spectrophotometer (FT-IR) were recorded as KBr pellets using perkin - Elmer 65 spectrophotometer (400 - 4000 cm^{-1}), Scanning Electron Microscopy (SEM, Neon-40, FESEM/FIB), electronic balance(ESj200 - 4), Energy Dispersive X- ray spectroscopy (EDX), Electrical grinding machine , pH meter (HANNA instruments, 210), oven, 100mL Volumetric flasks (PYREX,UK), pipette, 50 mL graduated cylinder, desiccators, Glass beakers, orbital shaker (SK 300), and 250 mL Stopper Conical flask.

3.3. Sampling of Raw Materials

A total of 5 kg each fresh banana and orange was obtained from Adama town, vegetable market, and 3 kg fresh turmeric was collected from Mizan Tepi agricultural institute. Adama is located at an altitude of 10° 42' 0" N and longitude 39° 34' 0" E Oromia region at an elevation of 1712 meters, 49 mile (79 km) southeast of Addis Ababa at, Ethiopia. The average annual temperature in Adama is 20.5 °C and about 808 mm of precipitation falls annually. Mizan tepi is located at an altitude of 7° 12′ N and longitude of 35°27′E with a mean elevation of 1,097 meters above sea level. The mean annually rain fall of the area ranges from about 1050 to 2160 mm.

3.4. Preparation of Adsorbents

The fruit materials were obtained from the local market and first peeled off to obtain the outer skin. The turmeric, banana and orange peels were washed with ordinary tap water and distilled water to remove possible foreign materials present (dirt and sands).The washed biomass was cut into small pieces (1-2 cm) and air dried for two week in air shade, followed by drying in an oven at 80 ºC for 2 hours without

grinding . The dried peels of banana, orange and turmeric were grounded using pestle and mortar followed by electrical grinding machine, to particle size fraction of 250 μm mesh size. The powdered fruit waste was mixed in equal proportion to yield adsorbents comprised of banana and orange (RBO), and banana, orange, and turmeric (RBOT). A portion of this mixed powder was chemically modified by using H_3PO_4 to yield chemically modified mix of (CMBO) and (CMBOT) as shown in Table 1. The dried powder then put in air tight bottles and stored in desiccators for further characterization analysis [70]. Special precautions must be taken during the collection of samples, the sample container must be thoroughly washed and well-rinsed with de ionized water routinely, dried, and stored in clean area to prevent contamination. Then, the collected sample was preserved by in refrigerator from the time of collection until analysis in laboratory.

Table 1 Designation and Composition of mixed fruit adsorbents

№	Adsorbent type	Mixed ratio	Mass in gram each adsorbents (g)	Total
1	CMBOT	1:1:1	33.33 , 33.33 , 33.33	100 g
2	RBOT	1: 1:1	33.33 , 33.33 , 33.33	
3	CMBO	1:1	50 : 50	
4	RBO	1:1	50 : 50	

Chemical modification of adsorbents: The crushed peel of each items were treated with H_3PO_4 to improve the efficiency of metal uptake and the same were done after mixing the crushed peels in equal proportion. In this study 100 g of dried fruit peel of each biomass and mixed fruit peels was treated with 1 L of (0.1M) H_3PO_4 for 48h with shaking at 100 rpm. After repeated decantation and filtration, the modified adsorbents were washed with distilled water and neutralized by 0.1 M NaOH until the pH value of solutions neutral. Then after, the modified adsorbents was then oven dried at 80^oC for 2 hour to constant mass, ground and sieved with 250 μm sieve size and it was put in air tight bottles and stored in a desiccators for further use in batch experiments and FT- IR and SEM - EDX analysis, [70].

3.5. Characterization of Adsorbent

3.5.1. Fourier Transform Infra Red Spectroscopy (FT -IR)

The adsorbent was characterized by using FTIR spectroscopy (perkin - Elmer 65 spectrophotometer) at Addis Ababa University to identify the functional groups of the prepared adsorbent materials before and after adsorption. The FTIR spectra of the adsorbent before and after adsorption of Cr (VI) were recorded in the range 4000 - 400 cm^{-1} with KBr discs.

3.5.2. Scanning Electron Microscopy (SEM- EDX)

Scanning electron microscopy (SEM, Neon-40, FESEM/FIB) analysis of mixed fruit was carried out in India, fruit waste peel powder samples before and after adsorption, to study its surface morphology and pore size using scanning electron microscope done at India. SEM has a high resolution, making higher magnification possible for closely spaced materials. The average pore size or diameter was also determined using SEM and elemental composition determined by EDX. Scanning Electronic Microscope (SEM), operating in variable pressure (VP) mode and 2 kV accelerating voltage was used for studying the surface morphology of the mixed fruit waste peel.

3.6. Preparation of Cr (VI) Stock solution

The standard stock solution of chromium (1000 mg/L) was prepared by dissolving 2.828 g of 99.9 % analytical grade $K_2Cr_2O_7$ in 1000 mL of distilled water. Standard working solutions of chromium with different concentrations were prepared from the stock solution by appropriate dilutions. 20(mg/L), 40(mg/L), 60(mg/L) and (80mg/L of chromium standard solution were prepared by diluting 20mL, 40mL, 60mL,and 80mL from 1000 ppm chromium stock solution with distilled water in 1000 mL volumetric flask (PYREX,UK) up to the mark respectively. The pH of aqueous solution was adjusted to the desired value by addition of 0.1 M HCl or 0.1M NaOH solution. The solution color turned to yellowish as shown in fig 6 and the reactions are as follows.

$$H_2CrO_4 \longrightarrow H^+ + HCrO_4^-$$

$$HCrO_4^- \longrightarrow H^+ + CrO4^{2-}$$

$$2HCrO_4^- \longrightarrow Cr_2O_7^{2-} + H_2O$$

Figure 4 Standard potassium dichromate stock solution

Estimation of Standard Calibration Curve: Standard solutions of chromium with different concentrations were prepared from the stock solution (from 1000mg/L) by appropriate dilutions. Calibration standards of (10 mg/L, 20 mg/L, 40mg/L, 60mg/L, and 80 mg/L of chromium standard solution was prepared by pipetting 10 mL, 20 mL,40mL, 60mL and 80 mL of 1000 ppm chromium stock solution with distilled water in 1000 mL volumetric flask up to the mark respectively used for calibrating the UV- visible spectrophotometer. For this purpose a 0.25% (w/v) solution of 1,5-diphenylcarbazide was prepared in 50 mL acetone. Each standard solutions (15mL) containing various concentrations of Cr(VI) was pipette out into 25mL standard flasks. To this 2mL of 3 M H_2SO_4 was added followed by 1 mL of 1-5 diphenylcarbazide and total volume was made up to 25mL using distilled water. After that the flasks was capped and mixed thoroughly by inverting several times. Then the mixture was allowed to stand for 10 minutes for full color development. Cr (VI) concentrations estimated by the intensity of violet color complex formed, was measured using UV - spectrophotometer at 540nm. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing. The same procedure was followed for the sample. Figure 5 is a calibration curve which is drawn between the initial known concentration and the value of absorbance measured from the UV-Vis spectrophotometer using 1, 5 DPC at 540nm. This is a linear curve passing through all point. This is the standard curve which is further used to find out the final concentration of Cr (VI) in the solution left after the completion of adsorption process. The following reaction scheme has been deduced for the reaction between Cr (VI) and DPC.

2 Cr (VI) + 3 DPC $\longrightarrow$ 2 Cr (III) + 3 Diphenylcarbazone

Cr (III) + Diphenylcarbazone $\longrightarrow$ 4 Cr (III) - Diphenylcarbazone

The Cr(III) diphenylcarbazone complex is responsible for the violet color that forms, with the intensity of the color being proportional to the concentration of chromium (VI) in solution and Cr(III) and diphenylcarbazone reacted in water.

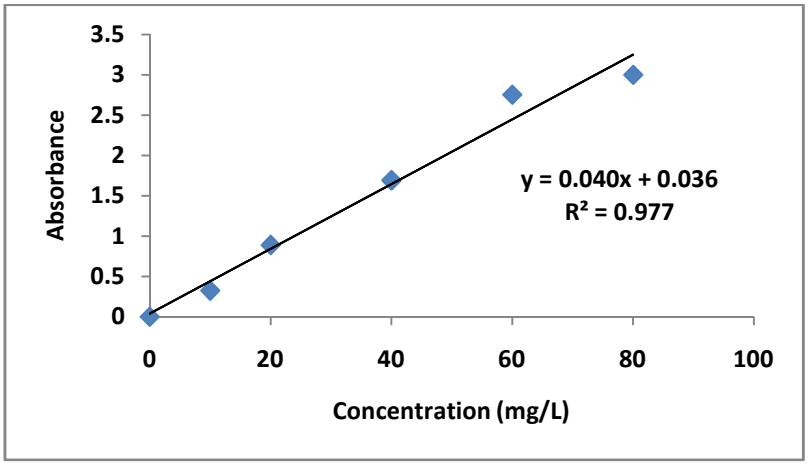


Figure 5 Calibration line for determination of Cr(VI) in the form of a complex with 1, 5-diphenylcarbazide

Full factorial design: Factorial design is used to test the effect of each factor. In factorial experiment, all possible combination of factor levels was tested. And it was determined the effects of individual factors and assessed the effect of change of variables for chromium removal full factorial design with four factor with each four / five/six level described in table (2)

Table 2 Full factorial deign experimental methods

Independent factors	Factors level
Concentration of chromium	Four (20ppm, 40ppm, 60ppm and 80ppm)
Dosage	For CMBOT and RBOT Six (0.2, 0.5, 1, 1.5, 2, 2.5 g) For RBO and CMBO five (0.2, 0.5, 1, 1.5, 2g)
Contact time	Four (30min, 60min, 90min and 120 min)
pH	Four (1,2, 3,4,5)
No of run	74
Replicate(two times)	2 * 74 = 148
Total experiment	198
Response	% removal = ((Co - Ce) / Co))* 100

3.7. Batch Equilibrium Studies

Preliminary test were done according to the method used by Arbind Kumar and Vipin Kumar [71]. 50 mL of Cr (VI) solution (60 mg/L) at the uncontrolled pH was taken in a 250 mL conical flask with a fixed dosage (1 g/L) of 250 µm size adsorbent for 60 min. The mixture was agitated on a shaker at a speed of 100 rpm at room temperature for a time which was sufficient for the chromium uptake process to reach equilibrium. Finally the residual chromium concentration was determined.

Batch adsorption studies was performed at room temperature at different pH (1 - 5), by keeping other factor constant, adsorbent dose (0.2, 0.5 , 1 , 1.5 , 2, 2.5 g), initial Cr (VI) concentration (20, 40, 60, 80 mg/L) and contact time (30min, 1 h, 1.5 h, and 2 h) to obtain the equilibrium data. All experiments were performed in duplicate. After attainment of equilibrium, the samples was filtered through 0.45 µm Whatman No. 1 filter paper and the residual Cr (VI) concentration in the filtrate was determined using the Uv - visible spectroscopy (T 80 + - PG Instrument Ltd) at 540nm using DPC.


a


b

Figure 6 a) PH Adjustment using Hanna PH 210 Micro Processor PH Meter b) mixture of adsorbent and adsorbate in a shaker model no SK 300

Chromium Removal Analysis: According to the method used by APHA, AWWA & WPCF [72]. UV-Visible spectrophotometer assisted with diphenyl carbohydrazide colorimetric method to measure chromium residue. A droplet of diphenyl - carbazide solution was added into the aliquot aqueous sample (coloring purpose) before it measured. After predetermined contact time adsorbent was decanted and separated from the solution using filter paper (using 0.45 µm whatmann filter) and the filtrate was analyzed. For this purpose a 0.25% (w/v) solution of 1,5-diphenylcarbazide was prepared in 50 mL acetone. Each sample solutions (15mL) containing various concentrations of Cr(VI) was pipette out into 25mL standard flasks. To this 2mL of 3 M H_2SO_4 was added followed by 1 mL of 1-5 diphenylcarbazide and total volume was made up to 25mL using distilled water. After that the flasks was capped and mixed thoroughly by inverting several times. Then the mixture was allowed to stand for 10

minutes for full color development. Cr (VI) concentrations estimated by the intensity of the violet color complex formed, was measured using UV -spectrophotometer at 540nm [72]. To assure data quality all the batch experimental points was duplicated.

Figure 7 T 80 + - PG Instrument Ltd UV- vis Spectrophotometer

3.7.1. Determination of Adsorption Efficiency

Adsorption measurement was made by batch technique at room temperature because of its simplicity and reliability. The batch adsorption studies were carried out at desired pH value, contact time and adsorbent dose. The amount of chromium adsorbed on mixed fruit peel known after comparing concentration of chromium before and after treatment. The amount of chromium per unit mass of composite fruit peel evaluated by the following mass balance equation.

$$qe = \frac{(Co - Ce)}{M} \times V \quad \ldots\ldots 10$$

Where M is the mass of adsorbent (g), Co = initiation concentration of chromium solution in mg/L, V = volume of chromium solution in liters, Ce = concentration of chromium solution at equilibrium (mg/L), qe = amount of chromium adsorbed on the fruit peel (mg/g). The percentage removal of chromium (VI) will be calculated as follows

$$\%\ \text{removal Cr(VI)} = \frac{Co - Ce}{Co} \times 100 \quad \ldots\ldots 11$$

The chromium mass adsorbed per gram of adsorbent was calculated by difference between the Cr^{+6} concentration of the solution before equilibrium and in the equilibrium, multiplied .

3.8. Optimization of Factors Affecting Chromium Adsorption

The parameters such as contact time, initial Cr (VI) concentration, PH, adsorbent dosage and contact time which affect the removal of Cr (VI) ions were optimized by varying each at a time while keeping the remaining parameters constant. The methods are presented as below.

Effect of pH on the Adsorption of Chromium ions:-To investigate the effect of pH on the adsorption of chromium ions, 1g of finely ground mixed chemically modified banana, orange and turmeric was weighed and put in a 250 mL conical flask. 50 mL chromium solution with concentrations of 60 mg/L was added to the flask and the mixture was shaked for duration of 1 hours with a constant agitation speed of 100 rpm at room temperature. The pH range of 1.0-5.0 (Table 7 & Figure 16) was used and chromium solution pH was adjusted by adding 0.1 M sodium hydroxide (NaOH) or 0.1M Hydrochloric acid (0.1 M HCl) before each experiment. The solution was then filtered using a Whatman filter paper No. 42(25 um) and the filtrate analyzed to evaluate the amount of chromium adsorbed using UV- Visible spectrophotometer at 540nm. The experiments were carried out in doublets and the average results were used for calculations. The same procedure was repeated for RBO, RBOT and CMBO.

Effect of dosage on the adsorption of chromium ions:-To investigate the effect of dosage on the adsorption of chromium ions, 0.2 g of finely ground chemically modified banana, orange and turmeric was weighed and put in a 250 mL conical flask at pH 2. 50 ml chromium solution with concentrations of 60 mg/L was added to the flask and the mixure was shaked at the speed of 100 rpm at room temperature. Repeat the same procedure for 0.5, 1,1.5, 2, 2.5 for 60 minutes. Then the samples were then filtered using a Whatman filter paper No.42 and the filtrate was analyzed to evaluate the amount of chromium in solution (Table 8 and figure 18). The above procedure was repeated for each of the other adsorbents (raw banana, orange and turmeric, chemically modified banana and orange and raw orange and banana peels).

Effect of initial concentration on the adsorption of chromium ions:-To investigate the effect of initial chromium concentration on the adsorption of chromium ions, 0.5 g of finely ground chemically modified banana, orange and turmeric was weighed, at pH 2 and put in a 250 ml conical flask. 50 mL chromium solution with concentrations of 20 mg/L was added to the flask and the mixture was shaked for duration of 60min with a constant agitation speed of 100 rpm at room temperature. This was repeated using 40, 60 and 80 mg/L concentrated solution. A pH value of 2 was maintained throughout the experiment by adding 0.1M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid solutions before each experiment. The solutions were then filtered using a Whatman filter paper No. 42

and the filtrate analyzed to determine the amount of chromium still in solution, from which the adsorbed chromium was calculated (Table 9 and Figure 19). The above procedure was repeated for each of the other adsorbents (raw banana, orange and turmeric, chemically modified banana and orange raw banana and orange and peels in 1:1 ratio).

Effect of Contact Time on the Adsorption of Chromium Ions:-To investigate the effect of contact time on the adsorption of chromium ions, 0.5 g of finely ground chemically modified banana, orange and turmeric was weighed and put in a 250 mL conical flask. 50 ml chromium solution with concentrations of 60 mg/L was added to the flask and the mixture was shaked at the speed of 100 rpm at room temperature for duration 30, 60, 90, 120, 150 minutes contact time. Then the samples were then filtered using a Whatman filter paper No.42 (Table 10 and Figure 20) and the filtrate was analyzed to evaluate the amount of chromium in solution. The above procedure was repeated for each of the other adsorbents (raw banana, orange and turmeric, chemically modified banana and orange and raw orange and banana peels).

3.9. Adsorption Isotherm and Kinetic Study

To establish the adsorption capacity of mixed fruit peel experimental data was fitted against two parameter isotherm equations such as Langmuir, and freundlich isotherm equations. The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface or to describe distribution of metal ions between the liquid phase and the solid phase. The isotherm results were analyzed using the Langmuir, and Freundlich isotherms. The kinetics of Cr (VI) ions adsorption process onto mixed waste peels was analyzed using pseudo-first-order and pseudo-second-order kinetic models. Adsorption kinetics is performed to evaluate both the equilibrium time and the rate of Cr(VI adsorption. The equilibrium time is one of the important parameters for subsequent adsorption isotherm studies. To evaluate the rate of Cr(VI) adsorption on adsorbents, the experimental data were analyzed using pseudo first and pseudo second order kinetic models. The pseudo second order model has been commonly used to describe chemical adsorption process of pollutants from aqueous solutions in recent study. Linear regressions are frequently used to determine the best fitting kinetic model.

Kinetic study:- Kinetic study was conducted by taking 50 mL of Cr(VI) solution with initial concentration of 40 mg/L in 250 mL conical flasks and adjusting the pH to 2. Then 0.5 g of CMBOT was added and the solution was agitated at 100 rpm in a shaker at room temperature. Solution was sampled at time interval of (10, 20, 30, 40, 50 min) for RBOT, CMBOT, RBO and analyzed. Experimental data were analyzed against kinetic models, which explain the mechanism of the adsorption processes. The same procedure was followed for CMBO for 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 min time interval with the same pH, concentration and dosage. The same procedure was followed by taking contact time.

Isotherm Study:- Equilibrium isotherms were studied by taking 50 mL of Cr(VI) solution (20 - 80mg/L) in 250mL conical flasks and solution pH was adjusted to 2. The 0.5g of CMBOT was added to the solution and agitated at 100 rpm for 60 min (equilibrium time) in electronic shaker at temperature of 25^{o}C. To establish the adsorption capacity of CMBOT experimental data was fitted against two parameter isotherm equations such as Langmuir, Freundlich, isotherm equations. The data was analyzed using UV-Visible spectropotmeter at 540nm. The same procedure was followed for CMBO, RBOT and RBO but for CMBO for 120min.

3.10. Data Analysis

All data generated from the above experiments was analyzed using the Microsoft word excel and the average of duplicate. Uv- Visible spectrophotometer was used for the determination of Cr(VI) ion using 1,5 DPC at 540nm. The curve-fitting tests for data points for isotherm, and kinetic studies were performed using Microcal Origin 8.0 software**.** Linear regression values were computed to obtain the best fit of kinetics and isotherm using Microsoft excel.

4. RESULT AND DISCUSSION

4.1. Adsorbent Characteristics Obtained from FT-IR Analysis

FTIR result of raw and chemically modified mix of banana and orange peel with and without turmeric measured at 400 - 4000 cm^{-1}displayed a number of absorption peaks as shown in Figure 8 and 9. As shown in the Figure 8 unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The broad peak at 3428, 3425, 3435, and 3421cm^{-1}indicated -OH and amine (-NH) – COOH groups of CMBOT, RBOT, CMBO and RBO, respectively.

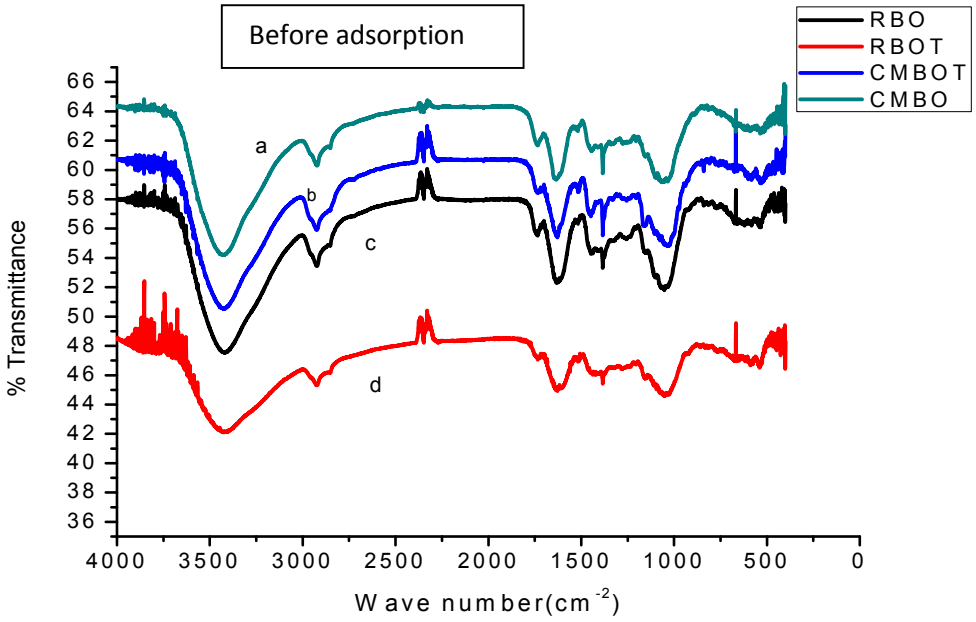


Figure 8 FTIR spectra (a) CMBO b) CMBOT c) RBO d) RBOT before loaded with Cr (VI)

After chromium adsorption (Figure 9) the peak was observed at 3430, 3413, 3417 and 3428 cm^{-1} for CMBOT, RBOT, CMBO and RBO, respectively. An increase in the intensity of the band at towards 3630 and 3428 cm^{-1} was the characteristic of OH elongations for CMBOT and RBO respectively. Before chromium adsorption stretching of the OH groups bound to methyl group presented in the signal at 2929, 2928 , 2929 and 2923 $cm^{-1}$for CMBOT,RBOT, CMBO and RBO and after chromium adsorption the peak observed at 2926, 2928, 2917 and 2925 respectively. The peak was diminished due to the involvement of functional group for adsorption.

As shown in Figure 8 the peaks was located at 1635, 1628, 1635, 1627 cm^{-1} are characteristics of carbonyl group(C═O) for CMBOT, RBOT, CMBO and RBO and the peak observed after chromium adsorption at 1636, 1636, 1643 and 1631 respectively. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biomass. The peaks observed at 1038, 1050, 1060 and 1052 cm^{-1} are due to C-H and C-O bonds for CMBOT, RBOT,CMBO and RBO as indicated in figure 8 and after chromium adsorption the peak was observed at 1032, 1033,1045 and 1055 respectively as shown in figure 9. CMBOT, RBOT, CMBO and RBO fruit peel which have OH, NH, carbonyl (C=O) and carboxyl (COOH) groups are important sorption sites. The above mixed fruit peels has those functional group that are responsible for the adsorption process.

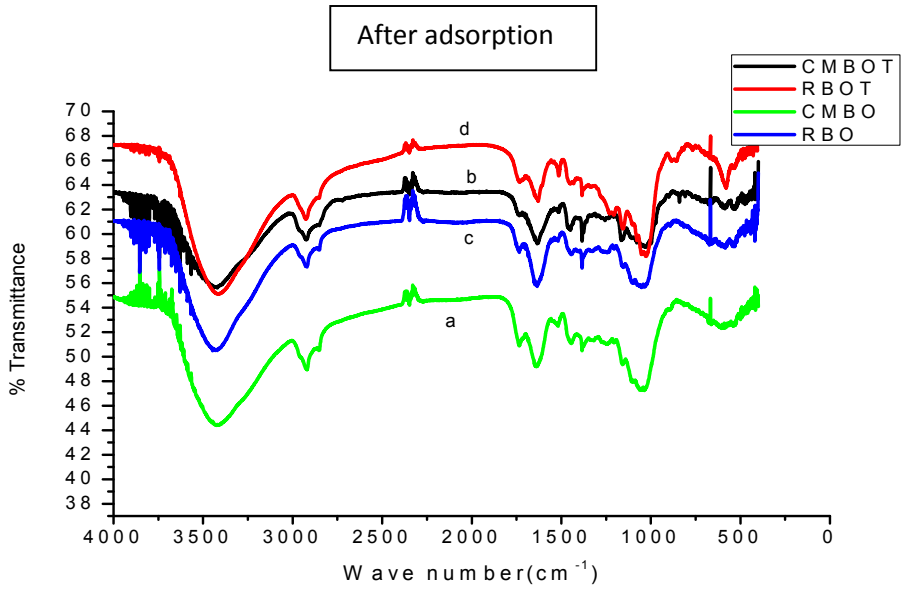


Figure 9 FTIR spectra (a) CMBO b) CMBOT c) RBO d) RBOT after loaded with Cr (VI)

The O-H stretching vibrations include cellulose, pectin, absorbed water, hemicelluloses, and lignin. C-H stretching vibrations include methyl, methylene, and methoxy groups[73].

Among the active groups, carboxylic acid and hydroxyl groups could play major role for chromium (VI) adsorption. Gottipati, [74] reported similar result on the removal efficiency of Cr(VI) by phosphoric acid treated bael fruit shell reported C-H stretching (aldehydes) observed at the peak 2850-3000 cm^{-1} played a very important role in Cr (VI) adsorption. Out of these, carboxylic and hydroxyl groups played a major role in the removal of Cr(VI) ions.

Similar results was also obtained by Candelaria Tejada -Tovar *et al.* [75] on comparison of banana peel biosorbents for the removal of Cr (VI) from Water. These results were expected due to the BP biomass contains polymers (hemicellulose, pectin and lignin) that are rich in organic functional groups such as COOH and OH. The adsorption capacity of acid treated CMBOT and CMBO depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface. The FTIR spectrum analysis of treated CMBOT and CMBO displays a number of functional groups on its surface indicating the complex nature of the adsorbent. A result indicated by (Ramos *et.al.* [76]) indicates Bonded -OH (hydroxyl) and C=O (Carbonyls) were strongly involved in Cr(VI) adsorption by phosphoric acid treated rice husk. Therefore, the broad and dominant absorption peak observed at 3500-3300cm^{-1} and 1760-1600cm^{-1} such as -OH (Hydroxyl) and C=O (Carbonyls) mainly involved in Cr(VI) adsorption on to CMBOT , CMBO, RBOT and RBO which was treated with phosphoric acid.

Generally from FTIR spectra of chromium ion loaded adsorbents it was observed that there was a shift in wave number of dominant peaks associated with the loaded chromium ion. This shift in the wavelength showed that there was a metal binding process taking place at the surface of adsorbents. There was a major shift in wave number from 3428 cm^{-1} for CMBOT to 3430 cm^{-1}for chromium ion loaded CMBOT peel. Also some of the metal binding groups present on the surface of adsorbents get diminished or disappeared after metal loading. Strong vibration peaks in between 3,500-3,000 cm^{-1}got diminished after chromium ion loading. Also C - O stretch of the -OH bend in range of 1,400 to 1,030 cm^{-1} almost disappeared from adsorbed adsorbents. Analysis of the FTIR provides the evidence that functional groups like carboxyl, hydroxyl, carbonyl and other aromatic vibrations were involved in chromium ion adsorption onto biomass surface. These groups in powdered CMBOT, CMBO, RBO and RBOT peel can be involved in chemical bonding and are responsible for the cation exchange capacity.

4.2. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscope (SEM), operating in variable pressure mode and 2.00 KV accelerating voltage was used for studying the surface morphology of the fruits peel. The surface characteristics, structure and particle size distribution of adsorbent before and after adsorption was examined using Scanning Electron Microscope (SEM). Figure 10a, b, c, d and 11a, b , c, d) shows the original SEM images of CMBOT, RBOT, CMBO and RBO peels in (50 X) electron beam before and after chromium adsorption. Figure 10b shows elliptical shape of CMBOT after chromium adsorption. Figure 10d show image of RBOT changed into rod shape after chromium adsorption because of the pore become filled with chromium and form aggregate. The SEM micrographs are shown in Figure 10 and 11 shows the CMBOT, RBOT and RBO which exposed the combination of small and large particles size, irregular, heterogeneous rough and porous surfaces with crater-like pores before the adsorption [76]. In raw banana and orange images there is agglomeration in comparison to acid treated banana and orange. The micrographs of the adsorbent present an unequal structure before metal adsorbed. Figure 11d shows CMBO shows homogeneous surface but the efficiency to bind metal ions is less in comparison to CMBOT. The exposure an availability of binding sites depends on particle shapes and sizes of adsorbent. The average pore size of CMBOT, RBOT, RBO and CMBO 33.10, 78.35, 516.33, 118.20 nm respectively. This image revealed that heterogeneous and porous surface except CMBO. Although all are good adsorbents but the removal efficiency of CMBOT is more in comparison to others followed by CMBO. This behavior can be attributed to the effective surface area increased as the particle size decreased [77]. The many pores on its surface support the adsorption process. After chromium adsorption which was partially covered by adsorbent, the pores became thicker and blocked. Similar structure and morphology were observed on orange peels [78]. The micrograph of fruit peel powder after Cr (VI) adsorption shows a reduction of number of pore space and surface area available. Hence, it is confirmed that there is metal adsorption on the surface of adsorbent. Similar work was done on the removal of Pb(II) from aqueous solution using fruits peel as a low cost adsorbent [42].

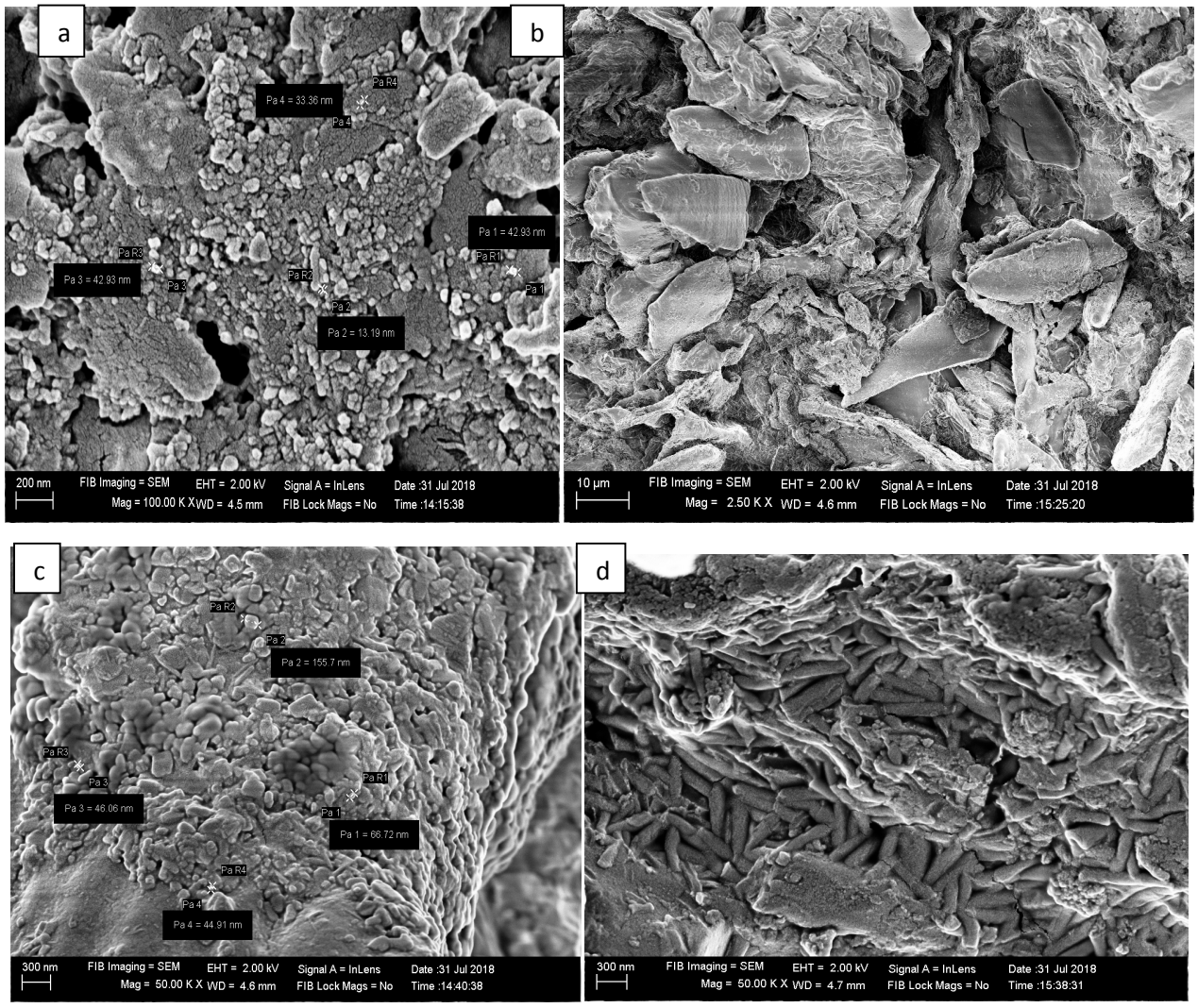
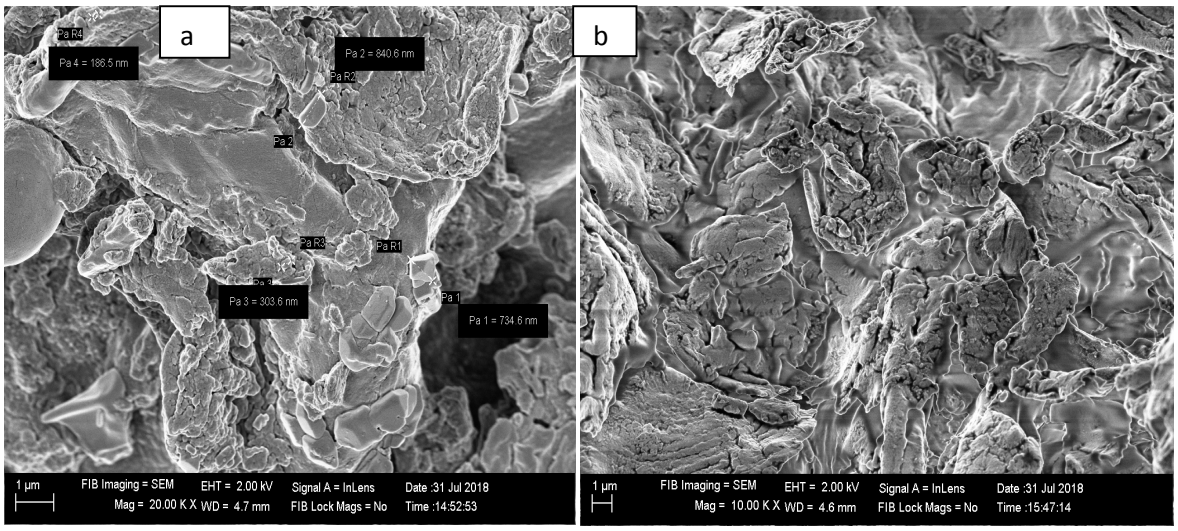


Figure 10 Scanning Electron micrographs of the fruit peel of (a) CMBOT before adsorption (50×) (b) CMBOT after adsorption (50×) c) RBOT before adsorption (50 x) d) RBOT after adsorption (50x)



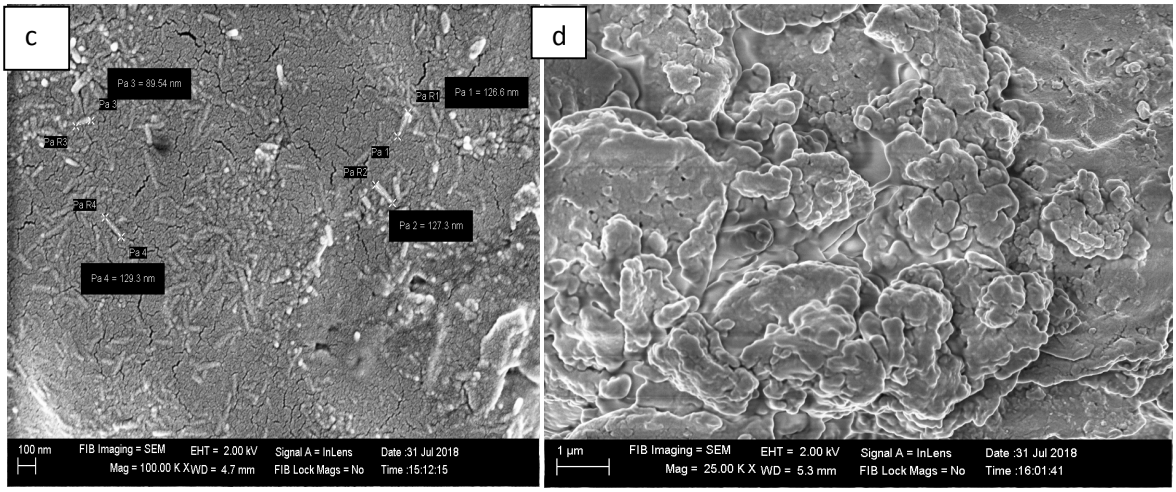


Figure 11 Scanning Electron micrographs of the fruit peel of (a) RBO before adsorption (20×) (b) RBO after adsorption (10×) (c) CMBO before adsorption (100×) (d) CMBO after adsorption (25.0×)

4.3. Energy Dispersive X-Ray (EDX) Analysis

Elemental analysis of mixed fruit adsorbent before and after chromium treatment was carried out using EDX. Untreated mixed fruit peel (Figure, 12 and 13,) revealed the presence of C, O, Si, P, Cl, Ca and K particularly intense peak of potassium. Turmeric contains large amount of Silicon as compared to banana. In comparison, chromium-treated mixed fruit peel (Figure 12a and 14a) had additional peaks confirming the sorption of chromium onto the surface. After chromium adsorption CMBOT phosphorus are not found due to overlapping of dominant functional group (Figure 12b). Figure 13c S and Si not found this is because of during paste preparation this elements are removed. After chromium treatment, changes in relative peak intensities were observed, especially for both Cl and K. This is ascribed to dissolution of KCl from the fruit peel, resulting in enhancement of the other elemental peaks, when placed into contact with the aqueous Cr(VI) solution. Most of Ca, S, P, K, S found in the banana peel and most of organic compounds found in orange peel and turmeric but especially turmeric contains terpene , flavinoids and phenols which are responsible for the chromium adsorption. But Ca and K also found in orange peel powder. Similar result was obtained by Jamil *et al*. [79]. Another study was also done by mandeep Kumar and CB Majumder [50] on the removal of Chromium (VI) from synthetic waste water by using acid treated banana Peel. Also Dr. A. M. Sabitha Rani and R. Saroja [80] preethy similar work was done on removal of hexavalent chromium from aqueous solution using chemically-modified sweet lime (*Citrus limetta*) peels. Table 3,4,5,6 shows the chemical constituent of mixed banana and orange with and without turmeric peels before and after chromium adsorption. Mixed fruit peel has more macro and meso-pores.

Table 3 EDX analysis of various constituents present on CMBOT adsorbent before and after chromium adsorption

CMBOT before chromium adsorption			CMBOT after chromium adsorption		
Element	Weight%	Atomic %	Element	Weight%	Atomic%
C K	53.42	61.84	C K	53.76	61.20
O K	41.67	36.21	O K	44.77	38.26
Si K	0.29	0.14	Si K	0.45	0.22
P K	1.70	0.76	-	-	-
Cl K	0.22	0.09	Cl K	0.37	0.14
K K	2.10	0.75	Ca K	0.18	0.06
Ca K	0.59	0.20	Cr K	0.47	0.12

*CMBOT - Chemically modified banana, orange and turmeric

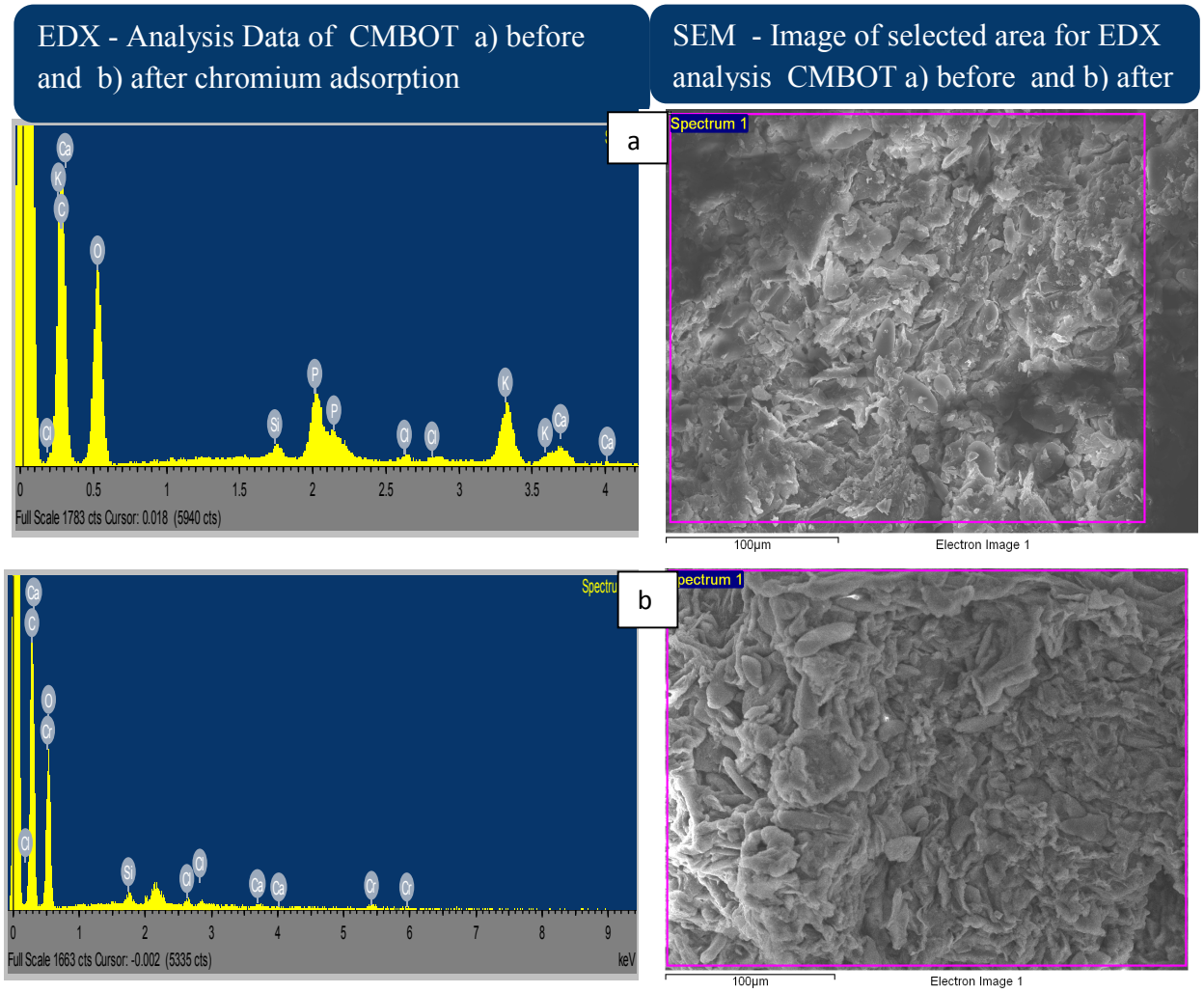


Figure 12 EDX spectrum of acid treated banana, orange and turmeric (a) before adsorption (b) after adsorption

Table 4 EDX analysis of various constituents present on raw banana , orange turmeric before and after chromium adsorption

EDX - RBOT before chromium removal			EDX- RBOT after chromium adsorption		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C K	58.41	65.68	C K	56.55	64.57
O K	40.03	33.79	O K	39.13	33.54
K K	1.39	0.48	Si K	1.04	0.51
Ca K	0.17	0.06	S K	3.04	1.30
			K K	0.16	0.06
			Cr K	0.06	0.02

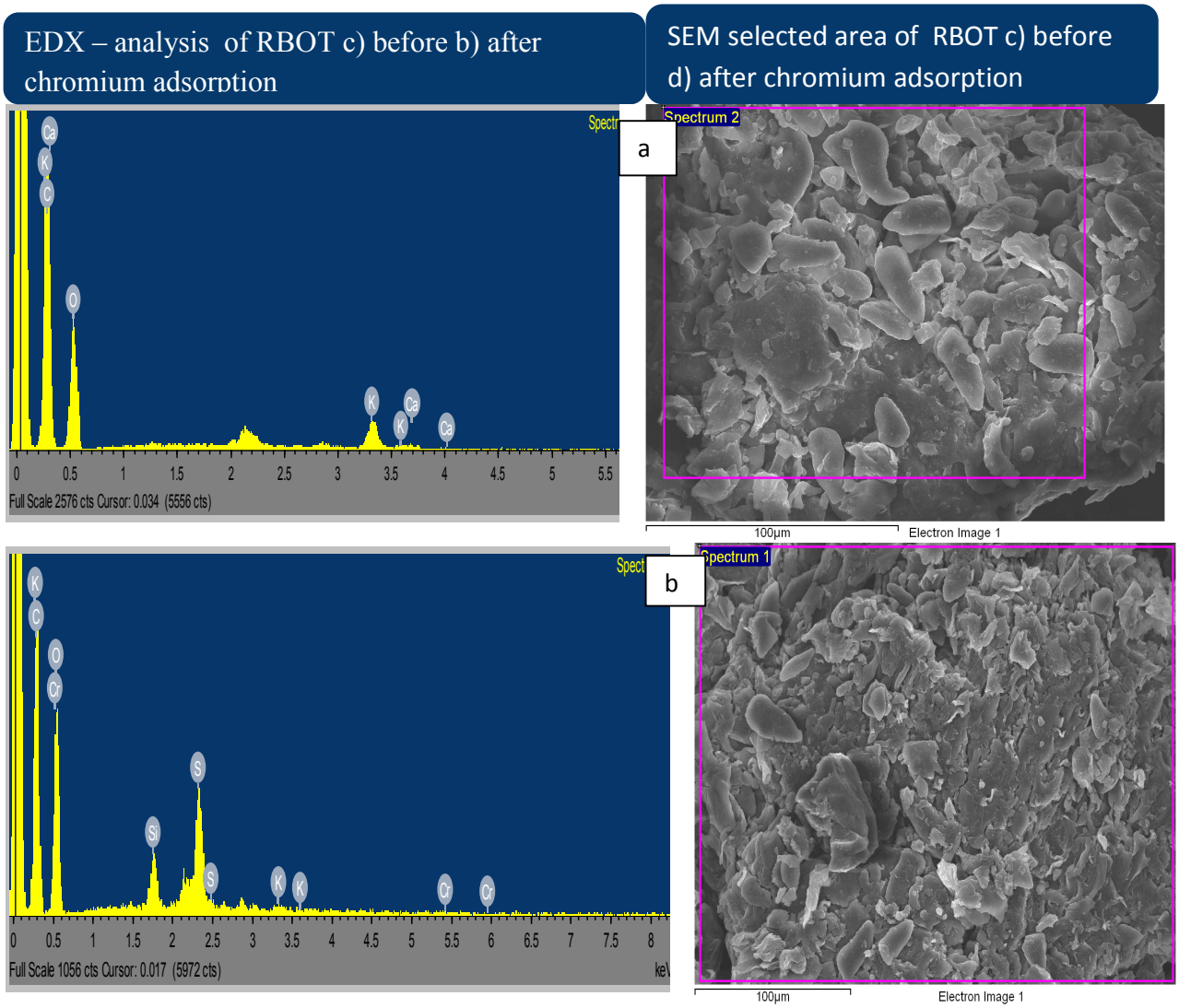
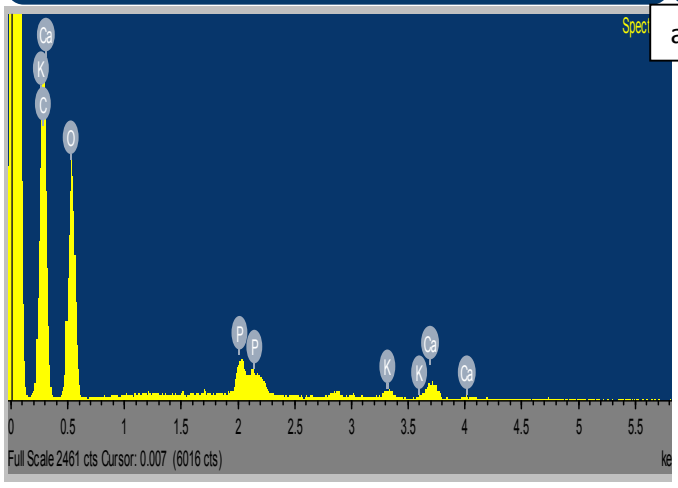


Figure 13 EDX spectrum of raw banana, orange and turmeric (a) before chromium adsorption (b) after adsorption

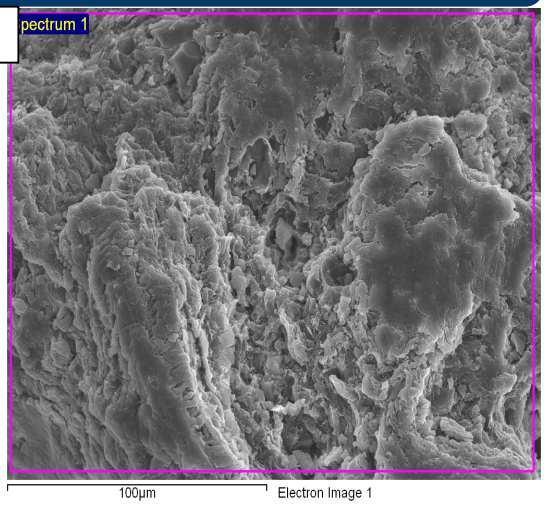
Table 5 EDX analysis of various constituents present on raw banana and orange before and after chromium adsorption

EDX of RRBO before chromium adsorption			EDX of RBO after chromium adsorption		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C K	53.31	60.84	C K	50.74	58.04
O K	44.89	38.46	O K	48.52	41.66
P K	0.88	0.39	P K	0.51	0.23
K K	0.28	0.10	Ca K	0.12	0.04
Ca K	0.65	0.22	Cr K	0.12	0.03

EDX - Data analysis of RBO before chromium adsorption



SEM – Image selected area of RBO before chromium adsorption



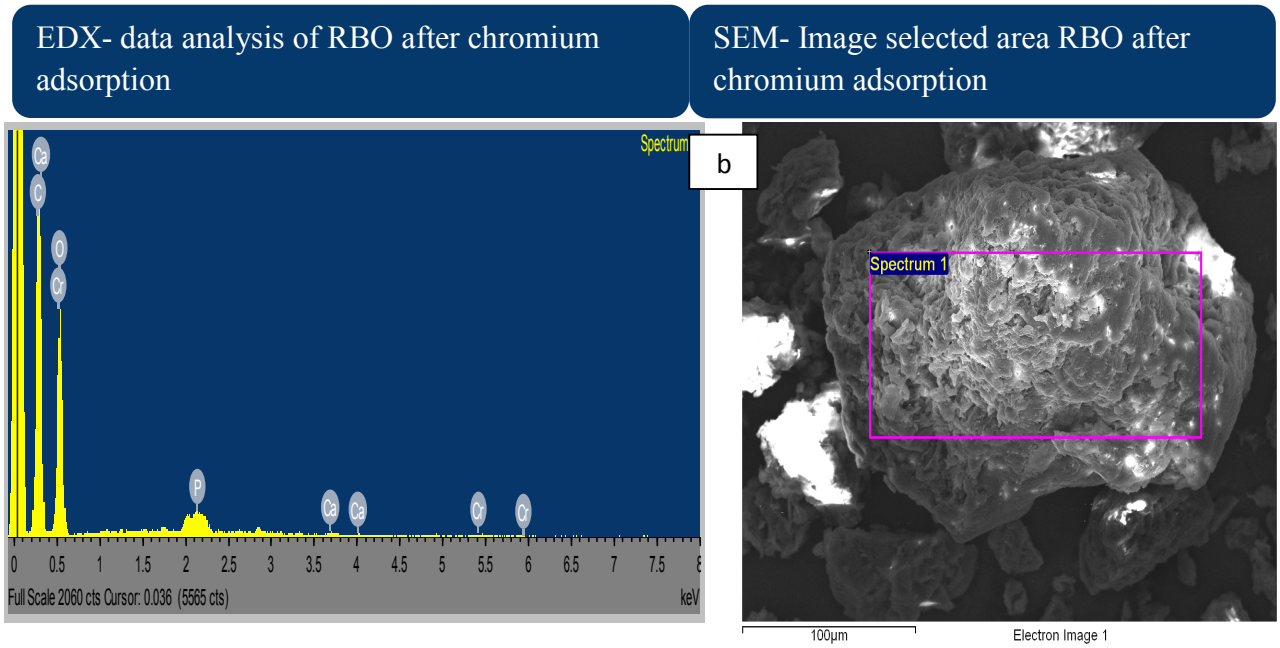


Figure 14 EDX spectrum of raw banana and orange (a) before chromium adsorption (b) after adsorption

Table 6 EDX analysis of various constituents present on chemically modified banana and orange before and after chromium adsorption adsorbent

EDX – Data analysis of CMBO before chromium adsorption			EDX- Data analysis of CMBO after chromium adsorption		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C K	54.87	62.75	C K	61.74	69.48
O K	42.16	36.20	O K	34.58	29.21
Cl K	0.27	0.10	Cl K	1.41	0.54
K K	2.00	0.70	K K	1.41	0.49
Ca K	0.71	0.24	Ca K	0.72	0.24
			Cr K	0.15	0.04

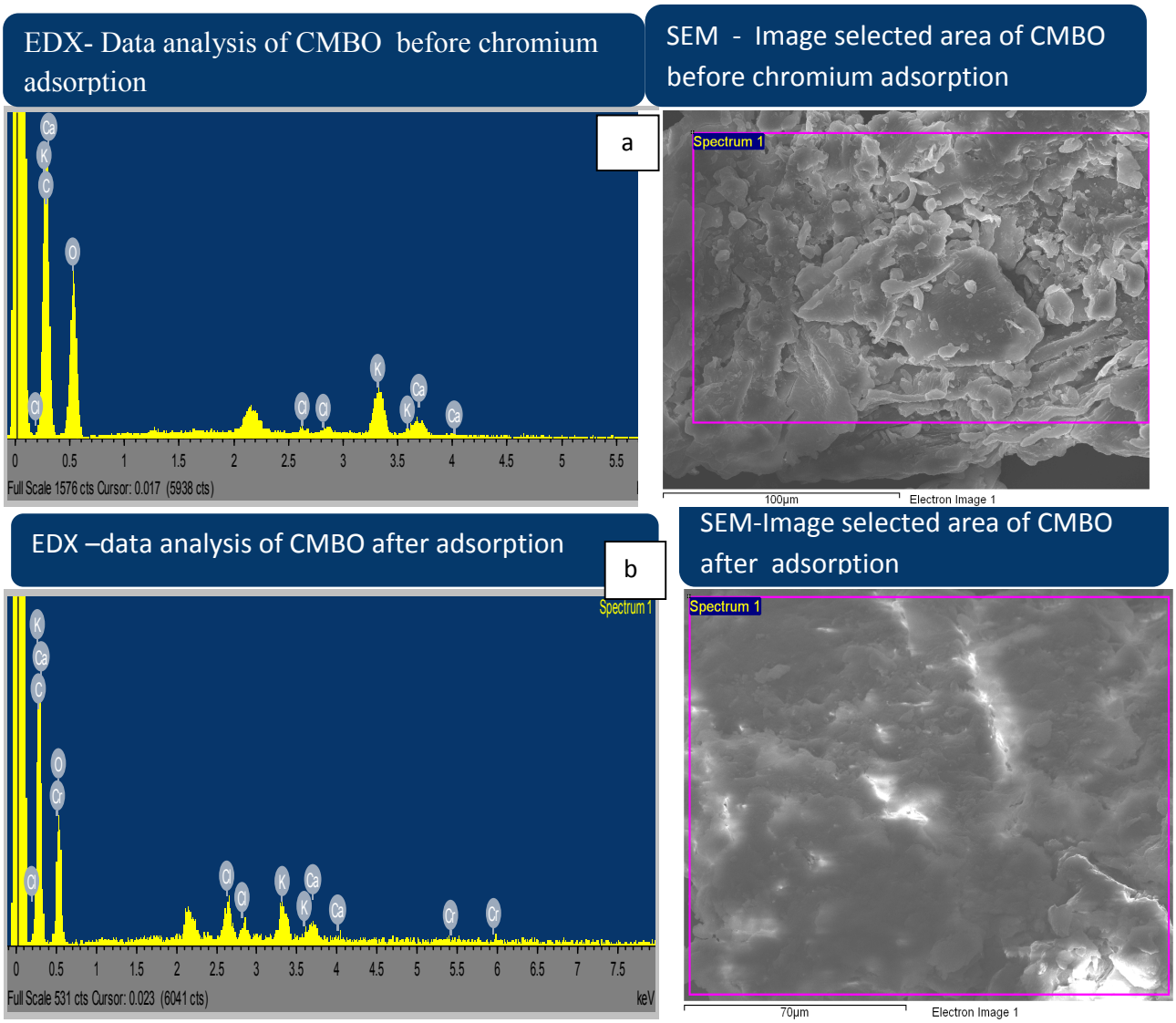


Figure 15 EDX spectrum of chemically modified banana and orange (a) before adsorption (b) after chromium adsorption

4.4. Result of Optimization of factors Affecting Chromium Adsorption

4. 4.1 Effect of pH on Cr (VI) Uptake

The pH of the solution affects the protonation of the functional groups on the adsorbent as well as the metal chemistry. The removal of Cr (VI) at different pH ranging from 1 to 5 was given in Figure 16. All other parameters were kept constant, i.e. chromium concentration (60 mg/L), adsorbent dosage (1g /50 mL), shaking speed (100 rpm), contact time (60 minutes), and at room temperature.

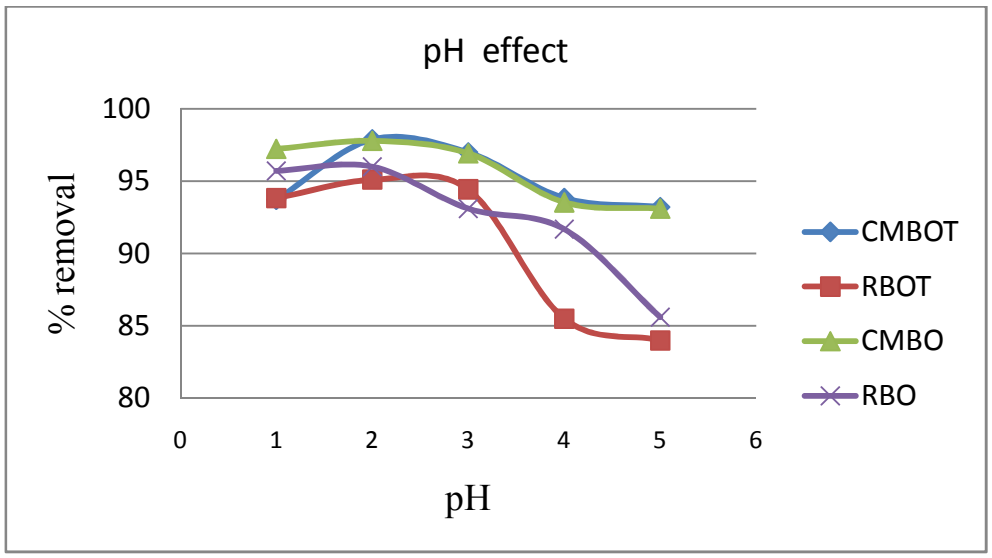


Figure 16 pH effect of Raw and modified banana ,and orange mixed adsorbent with and without turmeric at 60 mg/L initial chromium concentration , 100 rpm , dose 1g /50 mL temperature 25^{o}C, and contact time 60 min at 25^{O}C

As shown in the figure 16 the removal of Cr (Vl) were reaches maximum at pH of 2 for all adsorbents and decreased by increasing the pH values up to 5.0.

Table 7 Effect of pH on the percentage removal of Cr (VI)

	CMBOT		RBOT		CMBO		RBO	
pH	qe	% removal	qe	% removal	qe	% removal	qe	% removal
1	2.81	93.71	2.82	93.83	2.92	97.23	2.87	95.71
2	2.93	97.89	2.85	95.1	2.93	97.78	2.88	96
3	2.91	96.98	2.83	94.43	2.91	96.92	2.79	93.1
4	2.82	93.83	2.57	85.5	2.81	93.53	2.75	91.68
5	2.79	93.21	2.52	84	2.79	93.1	2.58	85.6

The removal of Cr (Vl) in the specified pH was in the order of CMBOT > CMBO > RBO > RBOT (Table 7). At pH 2, maximum removal efficiency about 97.89% was obtained for CMBOT followed by CMBO (97.78%) and RBO (96%) , the least were recorded for RBOT (95.1%).This implies at pH 2, due to the excess amount of H^+ ions within the medium of CMBOT and CMBO, the active site on the absorbent positively charged. This causes a strong attraction between these sites and negatively charged $HCrO_4^-$ ions. Also in RBOT and RBO removal efficiency was low because of several viscous compounds such as lignin and pectin occupy the pores of cellulose fibers [81]. Chemical modification using H_3PO_4 can open this pore. Therefore the removal efficiency was increased in case of CMBO and CMBOT. The initial pH of solution is an important operating variable in the adsorption process chromium using adsorbents made from mixed fruit waste as it influence ion speciation and/or surface properties of the adsorbents [82]. For instance, decreasing pH may favor hydroxyl groups in lignocellulosic wastes to diffuse into the solution, so, it would be more probable for $Cr_2O_7^{2-}$ions to be adsorbed on available adsorption sites. The other possibility may be at lower pH, the adsorbent is positively charged due to protonation resulting in electrostatic attraction with the dichromate [83]. After the active sites of the adsorbent gets exhausted, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles, which is a function of solution and the dominant chromium species co-exist in various forms, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, and , H_2CrO_4, CrO_4^{2-} of which $HCrO_4^-$ predominates in the acidic pH [84]. Maximum adsorption at pH 2.0 indicates that it is the $HCrO_4^-$ form of Cr (VI) which is adsorbed partially on the Acid treated banana, orange with and with out turmeric. At acidic pH 2, in which higher level Cr(VI) elimination was observed, adsorbent surface is highly protonated, facilitating $HCrO_4^-$ anion removal as a result of electrostatic interaction based adsorption. However, surface protonation decreases when pH is increased. There is strong competition between CrO_4^{2-} and OH^- species present at high pH values. Thus, the number of positive sites on adsorbent surface becomes reduced at high pH, showing a decrease in Cr(VI) removal capacity [63]. Relatively Similar results were reported by Ali et al. [49] at PH 3 for Cr (VI) removal using chemically modified banana peels, they pointed out that at higher pH the surface of adsorbent becomes negatively charged while at lower pH, the adsorbent surface is protonated improving electrostatic attractions with oxyanions of hexavalent chromium. Candelaria Tejada-Tovar et al. [75] reported that comparison of Banana Peel adsorbents for the removal of Cr (VI) from water at PH 3. The removal effecency was 93.5% which is less than the present work. At optimized condition it was 99.83 %, 99.75 % ,96.5 % and 96.33 % for CMBOT, CMBO, RBO, RBOT at pH 2 respectively.

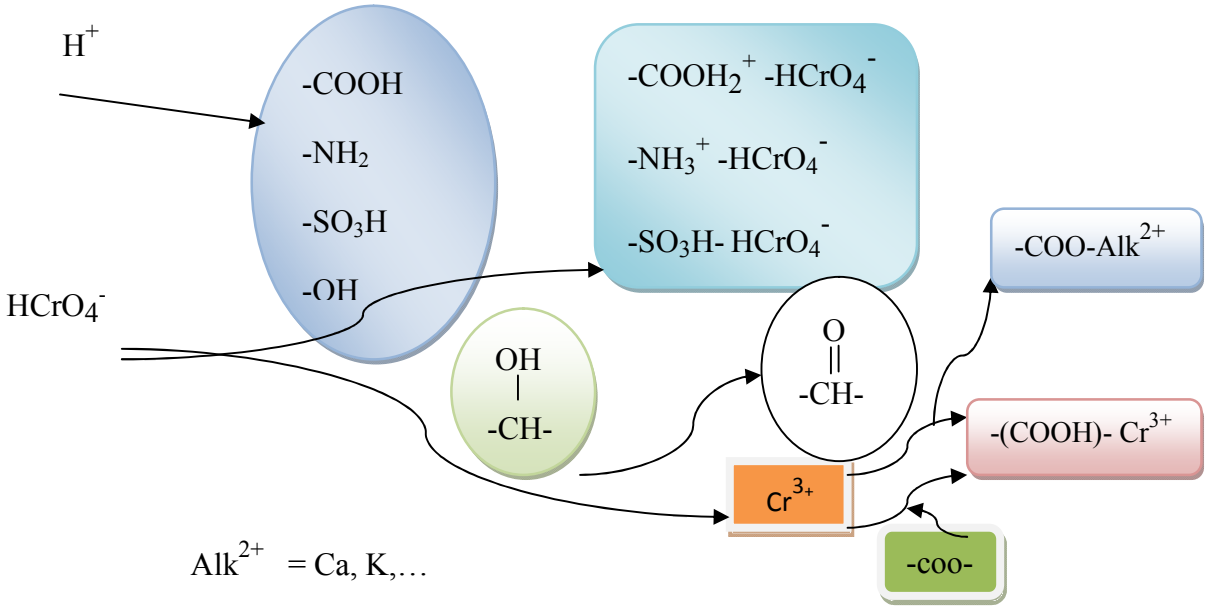


Figure 17 Result of Chromium (VI) adsorption mechanism and reduction with different functional group of mixed fruit peel

From the above experimental results and the instrumental analysis, the adsorption mechanisms are proposed as shown in Figure 17. The removal of anionic hexavalent chromium is a complicated process, in which reduction, surface complex formation, and ion exchange are involved. Hexavalent chromium can form surface complexes with the protonated functional groups on the adsorbents, such as -COOH, -NH_2, -OH and -SO_3H. The Cr(VI) anions can also oxidize the secondary alcohol groups on the adsorbents, while being reduced to Cr(III) cations. The Cr(III) cations that formed from the redox reactions are then able to undergo ion exchange reactions with cationic alkaline metal ions (Alk in Figure 17) such as $Ca^{2+}$and K which are initially bound onto the adsorbents. Experimental evidences reported in the literatures have demonstrated that Cr(III) ions are accumulated on the fruit peel due to ion exchange. In addition, the carboxyl group can form metal complex due to coordination reactions.

4.4.2 Effect of adsorbent dosage on Cr (VI) uptake

The effect of adsorbent dosage on the removal of chromium (VI) at room temperature was investigated by varying the amount of adsorbent from 0.2 to 2.5 g/ 50 mL and agitated at 100 rpm for 60 min using initial Cr (VI) ion concentration of 60 mg/L and at pH value of 2.0 was given in Figure 18.

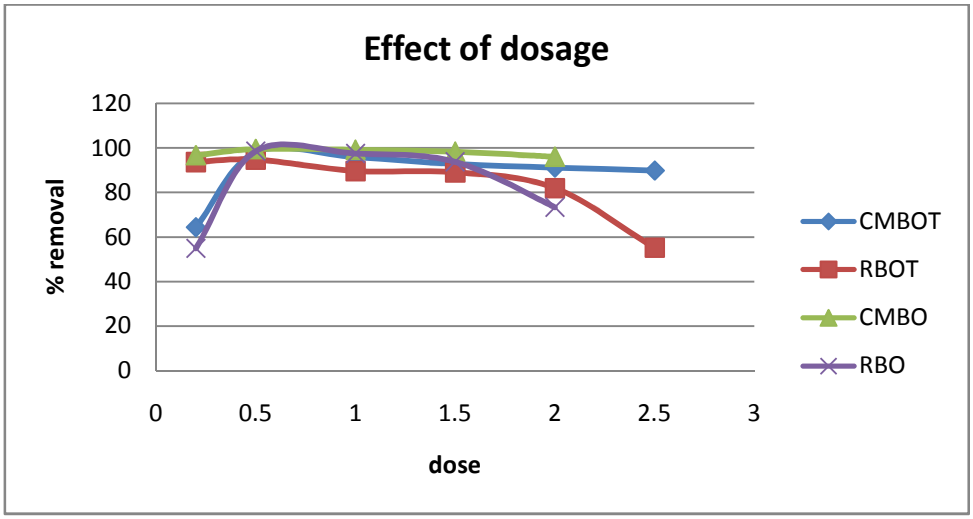


Figure 18 The effect of adsorbent dose on removal efficiency at initial conditions of Cr(VI) concentration = 60 mg/L, pH = 2, contact time = 60 minute, Agitation speed = 100 rpm at 25^{O}C.

As illustrated in Figure 18 the results indicate that the percent removal of chromium (VI) increased with the increase in the amount of adsorbent and the removal efficiency for chemically modified mixed waste peel was better than that of the raw fruit waste peel.

Table 8 Effect of adsorbent dose on the percentage removal of Cr (VI)

	CMBOT		RBOT		CMBO		RBO	
Dosage	qe	%removal	qe	%removal	qe	% removal	qe	%removal
0.2	9.65	64.35	14.05	93.65	14.5	96.67	14.45	54.92
0.5	5.9	98.1	5.68	94.7	5.99	99.5	5.91	98.5
1	2.86	95.85	2.69	89.6	2.98	99.23	2.92	97.46
1.5	1.86	92.78	2.26	89.03	1.96	98.31	1.87	93.71
2	1.38	91.18	2.46	81.93	1.5	96.02	1.1	73.33
2.5	1.08	89.81	1.65	55.12	ND	ND	ND	ND

ND = Not determined

As shown Table 8 the highest uptake was obtained at adsorbent concentration of 0.5 g/ 50 mL for all adsorbents at 98.1%, 99.52 %, 98.5 % ,and 94.65% uptake for CMBOT, CMBO,RBO and RBOT respectively . Jeyaseelan and Gupta [63] observed similar results with the removal efficiency reaching a constant value at 0.8 g/ 50 mL adsorbent dosage of green tea leaves of Camellia sinensis plant species. The results obtained obviously follow such a trend due to more adsorption sites being available with the

as amount of adsorbent increases. Since adsorption sites adsorbent particles increase, it would be more probable for $HCrO_4^-$ and CrO_4^{-2} ions to be adsorbed and thus adsorption efficiency should also increase as reported by Bansal *et.al* [85]. In this particular case, the concentration of the Cr(VI) ions is constant and therefore increasing the adsorbent dosage increases the available adsorption surface area. Also the decrease in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. The limiting constant maximum removal capacity could be explained from the fact that all adsorbents have a finite number of active sites which should become saturated at some adsorbate concentration. However at higher dosage, the number of such sites per unit mass comes down because of aggregation and thus flocculation of adsorbent particles [86]. Such aggregation would lead to a decrease in the total surface area of the adsorbent. In the other hand, further increase of dosage of biomass result in decreased of total chromium ion adsorption. This was because after occupying most of the available site, the remaining vacant surface sites were difficult to be occupied due to the repulsive forces between chromium ion (VI) adsorbed on the biomass and solution phase [87]. In brief, suitable operational conditions, recommended for further experiments, are pH 2 and dosage 0.5 g/ 50mL for CMBOT, CMBO, RBOT and RBO Peel.

4.4.3 Effect of initial metal concentration on Cr (VI) uptake

Effect of initial Cr (VI) ion concentration on its removal was carried out at optimized adsorbent dose (0.5 g / mL) and pH (2.0) for 60 min at room temperature by varying the metal ion concentration from 20 - 80 mg/L as shown in Figure 19.

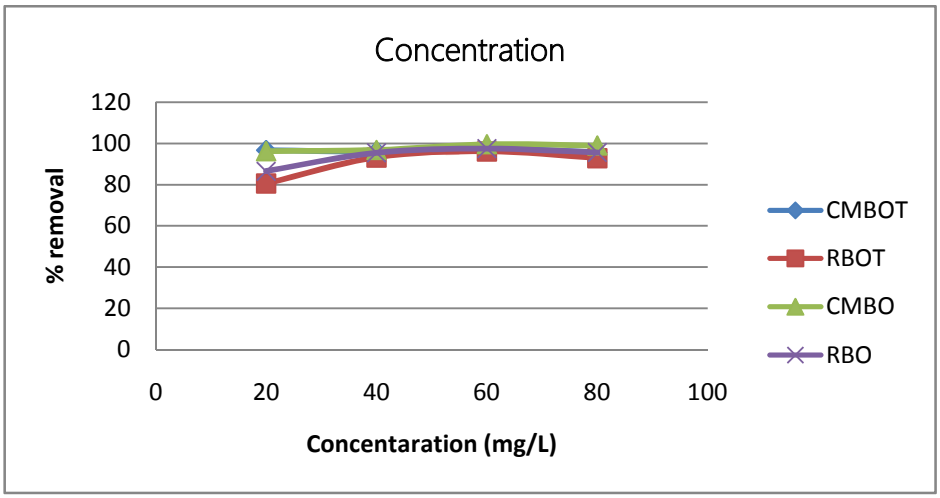


Figure 19 The effect of initial Cr (VI) concentration at initial conditions of adsorbent dose =0.5 g/50 mL, pH = 2, contact time = 60 minute, Agitation speed = 120rpm at $25^{O}C$

As shown Figure 19 at lower Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of the initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. Removal efficiency in mg/g showed different trends than that of percent adsorption (Figure 19). Increase in the initial concentration up to a certain point show an increasing removal of chromium as much as available active sites [38]. However, further increase in the adsorbate results in the reduction of removal efficiency since all the active sites have already been occupied by the metal ions. The percentage of Cr (VI) ions uptake for the four adsorbents increased with the initial metal concentrations as expected and remained nearly constant after equilibrium time as shown in Figure 19.

Table 9 Effect of initial concentration on the percentage removal of Cr (VI)

	CMBOT		RBOT		CMBO		RBO	
Conc.	qe	%removal	qe	%removal	Qe	%removal	qe	% removal
20	1.93	96.63	1.61	80.5	1.92	96.19	1.73	86.5
40	3.84	96.06	3.73	93.18	3.871	96.78	3.82	95.5
60	5.85	97.54	5.77	96.08	5.97	99.58	5.85	97.46
80	7.77	95.52	7.68	96.00	7.938	99.24	7.65	95.59

Table 9 shows the adsorption efficiency 97.54% , 96.08%, 99.58% and 97.46 % CMBOT ,RBOT, CMBO and RBO respectively. As the metal ion concentration decreases, the percent removal increases. This may be due to the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent. Generally from Figure 19 and Table 9 showed that the adsorption was rapid in the initial stages up to 60 mg/L and gradually decreased with progress of adsorption. Similar results were obtained by Namasivayam *et.al* [88] This can be attributed to the saturation of sorption sites on adsorbents. The initial concentration provides a significant driving force to overcome all mass transfer resistance of metals ion between aqueous and solid phases. Hence, a higher initial concentration of Cr (VI) increased the rate of adsorption [89].

4.4.4 Effect of contact time on Cr (VI) uptake

The time required for the adsorption of Cr (VI) on 0.5 g / 50 mL mixed raw and chemically modified banana , orange and turmeric peels with and without turmeric equilibration were studied. The initial concentration was kept constant at 60 mg/L and pH was set at 2.0. The experimental data indicate that Cr (VI) ion adsorption increased with increasing contact time. This is due to prolonged contact between the adsorbent surface and the chromium ion as shown in Figure 20.

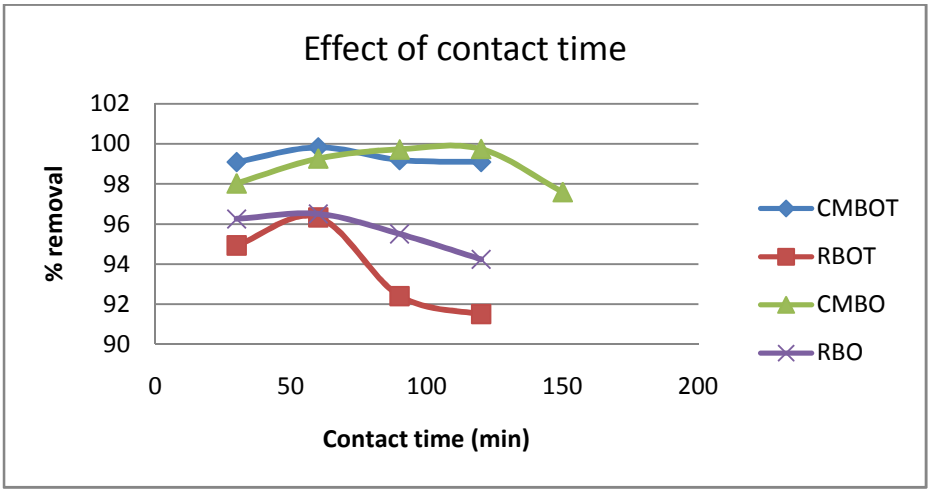


Figure 20 The effect of contact time at initial conditions of Cr(VI) concentration = 60 mg/L, adsorbent dose = 0.5 g, pH = 2, contact time = 60 minutes, agitation speed =100 rpm at 25^{O}C

Figure 20 shows that adsorption capacity sharply increased with increase in time and attains equilibrium in 60 min for the three adsorbents (CMBOT, RBO and RBOT), 120 min for CMBO.

Table 10 Effect of contact time on the percentage removal of Cr (VI)

	CMBOT		RBOT		CMBO		RBO	
Time(min)	qe	% removal	qe	%removal	qe	%removal	qe	%removal
30	5.946	99.1	5.696	94.93	5.88	98.03	5.77	96.25
60	5.99	99.83	5.78	96.33	5.96	99.27	5.79	96.5
90	5.95	99.2	5.57	92.4	5.984	99.73	5.73	95.5
120	5.95	99.1	5.48	91.5	5.99	99.75	5.7	94.23
150	ND	ND	ND	ND	5.86	97.6	ND	ND

ND =Not determined

Table 10 shows that the maximum adsorption capacity of CMBOT, CMBO, RBO and RBOT, was 99.83%, 99.75%, 96.5% and 96.33%) respectively. The rate of adsorption is higher within the first 30 min due to large available surface area of the adsorbent and a high concentration gradient. After the active sites of the adsorbent gets exhausted, when equilibrium is attained, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [90]. However with increasing contact time, the bringing energy between Cr and adsorbent was found to be less than equilibrium constant and, hence desorption was observed resulting in negative adsorption. Lower adsorption rate in the latter stage (after 60 min for CMBOT, RBO and RBOT and 120 min for CMBO was due to the difficulty encountered by Cr ions in occupying the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk phase [91]. This may also be due to intraparticle diffusion process dominating over adsorption. The results also indicate that CMBOT > CMBO > RBO > RBOT in order of adsorption capacities. This is because chemical modification results in exposure of more binding sites for chelating adsorbate species in relatively shorter interval of time with even better efficiency. For CMBOT, RBOT and RBO contact time at 150min was not determined because equilibrium was maintained with 60min. After 60min the removal efficiency was decreased. For CMBO equilibrium was maintained at 120min. After 120min removal efficiency of CMBO decreased.

4.5 Adsorption Methods

4.5.1 Adsorption kinetics

In order to understand mechanism of adsorption and potential of rate controlling step, numbers of kinetics models have been used to determine experimental data of Cr (VI) adsorption. The first kinetic model applied for experimental data was pseudo first because it has been widely used to predict metal adsorption kinetics of solid/liquid system. The pseudo-first-order kinetic model can be expressed linearly as [68].

$$\ln(qe - qt) = \ln qe - k1t \quad \ldots\ldots 12$$

In order to examine the controlling mechanisms of adsorption process the data was analyzed using pseudo-first-order. The results are displayed in the Figure 21. where, k1 rate constant (min^{-1}) of pseudo- first order kinetic equation, qe and qt, quantities of adsorbate adsorbed at equilibrium and at some time ($mg\ g^{-1}$). Hence a linear hint predictable among the two limits ln (qe - qt) and t which gives the result about kinetics model, shown in Figure 21.

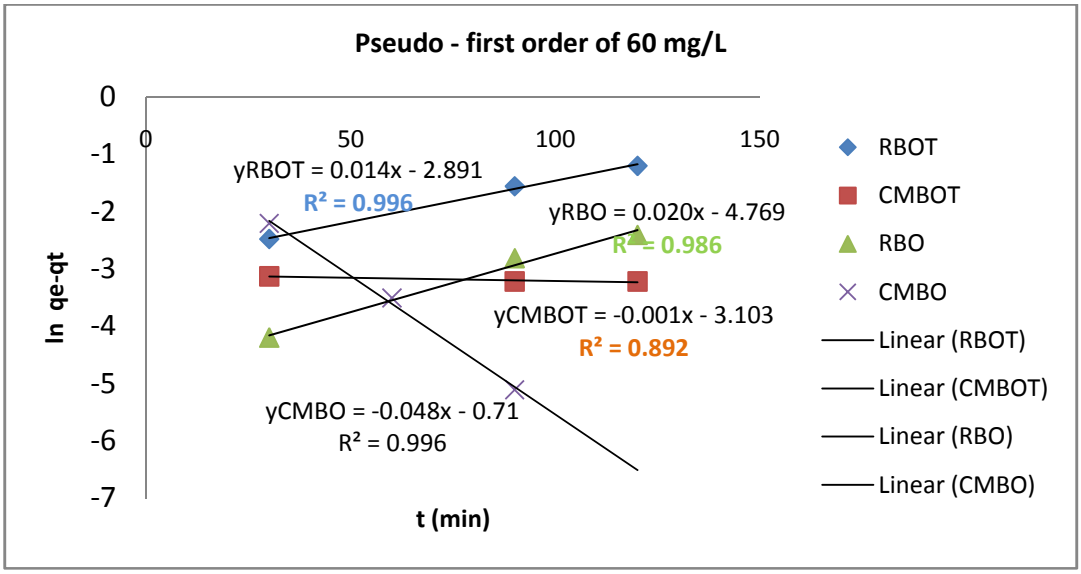


Figure 21 Pseudo-first order kinetic plots for the adsorption of Cr (VI) onto RBOT, CMBOT, RBO and RBO, at optimum condition with concentration of 60 mg/L

The values of k_1 and qe can be determined from the slope and intercept and value of k_1, qe and R^2 is given in Table 11.

Table 11 Value of k1, qe and R^2 for pseudo first order kinetic model (60mg/L)

Pseudo First order kinetic model (60mg/L)				
Adsorbents	$K_1(min^{-1})$	qe calc(mg/g	qe expl(mg/g	R^2
RBOT	-0.014	0.014	5.78	0.996
CMBOT	0.001	0.0449	5.99	0.892
RBO	-0.02	0.000849	5.79	0.986
CMBO	0.048	2.034	5.99	0.996

The adsorption may also be described by pseudo-second order kinetic model if the adsorption does not follow the first order kinetics. Pseudo- second order kinetics is the other type of adsorption kinetics that has been successfully applied to metal ions and organic substance. It state that the slowest step is chemical adsorption [69].The linearzed form of its equation is expressed as;

$$\frac{dq}{dt} = k2(qe - qt) \quad \text{.....13}$$

After integrating equation for boundary condition the equation becomes

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe} \quad \text{.....14}$$

Where K_2 = second order rate (g/mg min) and h = $K_2 qe^2$ is initial adsorption rate.

The values of (t/qt) were linearly correlated with t. The plot of (t/qt) vs. t (Figure 22) gives a linear relationship from which $k_1$and qe can be determined from the slope and intercept of the plot, respectively.

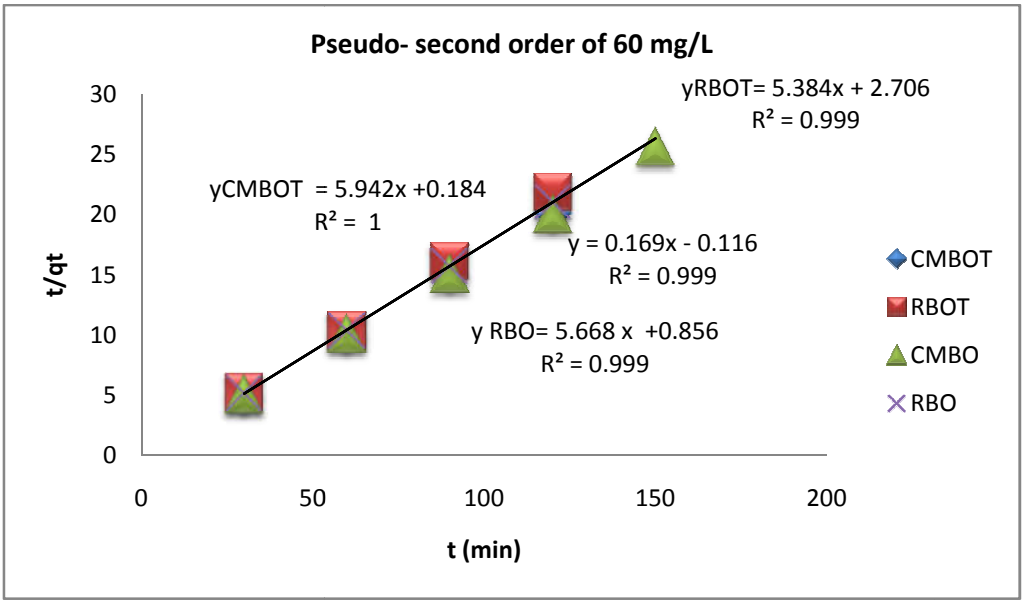


Figure 22 Pseudo-second order kinetic plots for the adsorption of Cr (VI) onto RBOT,CMBOT, RBO and RBO, at optimum condition with concentration of 60 mg/L

The corresponding linear regression correlation coefficients R^2 are given in table 12

Table 12 Value of k_2, qe(cal)and R^2 for pseudo second order kinetic model (60mg/L)

Pseudo second order kinetic model (60mg/L)				
Adsorbents	K_2 (g/mg min)	Qe calc(mg/g)	Qe expl(mg/g)	R^2
CMBOT	192	0.168	5.99	1
CMBO	0.223	6.06	5.99	0.999
RBOT	0.069	0.185	5.75	0.999
RBO	3.453	0.176	5.79	0.999

Results in Table 12 show that in the chromium metal ions, R^2 values of pseudo second model order fits better with the experimental data than pseudo first order model. Calculated equilibrium adsorption capacity q_e(cal), pseudo second order rate constant and the initial adsorption rate were obtained from the model.The experimental equilibrium adsorption capacity and the calculated capacity are close to

each other as can be seen from the Table 12 with the R^2 value for all the chromium ions are greater than 0.999, this shows the suitability of this model. This suggests that Cr (VI) ions are attached to the adsorbent surface by complexation and ion exchange. That is, chromium ions can bind to two binding sites on the mixed fruit surface. The chemically modified forms of the adsorbents recorded the higher values of qe and K_2 as compared to the raw forms RBO and RBOT. The model is based on the assumption that chemisorption is the rate limiting step [11- 92]. Similar fit to this model has been also reported by Wu *et al.* [93] for adsorption of trivalent chromium in lignin. Similar results were obtained as shown Table 13, Figure 24 as compared to pseudo first order at 40 mg/L.

Table 13 Value of k_1, qe (cal)and R^2 for pseudo first order kinetic model (40 mg/L)

Pseudo first order kinetic model(40 mg/L)				
Adsorbent	K1	Qe(calc)	Qe (expl)	R^2
RBOT	0.065	2.45	3.84	0.712
CMBOT	- 0.003	0.0178	3.965	0.046
RBO	- 0.018	0.804	3.85	0.599
CMBO	0.009	0.069	3.98	0.131

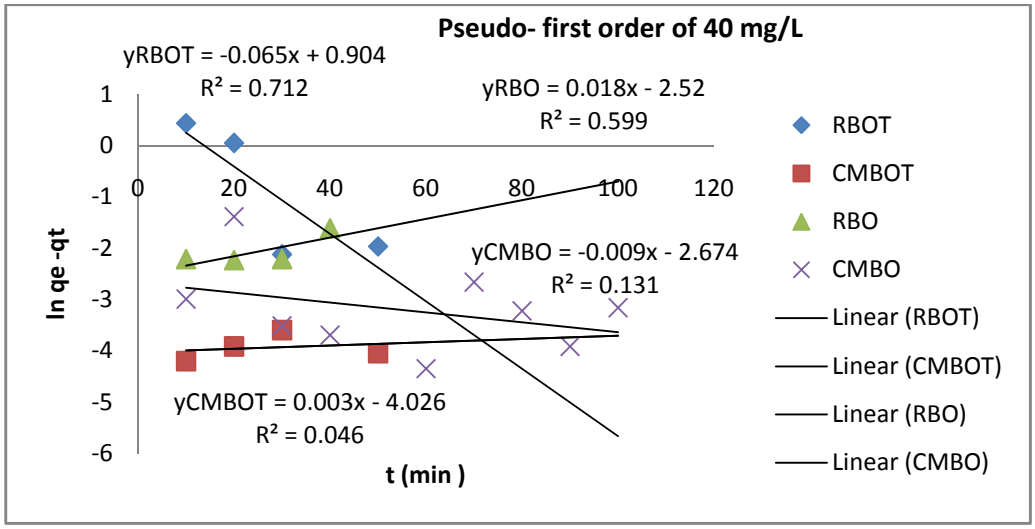


Figure 23 Pseudo-first order kinetic plots for the adsorption of Cr (VI) onto RBOT, CMBOT, RBO and CMBO at optimum condition concentration of 40mg/L

Table 14 Value of k_1, qe (cal)and R^2 for pseudo second order kinetic model (40mg/L)

Pseudo second order kinetic model(40 mg/L)				
Adsorbent	K_2	Qe cal	Qe expl	R2
RBOT	0.021	4.651	3.85	0.975
CMBOT	9.14	3.953	3.965	0.999
RBO	0.095	3.086	3.85	0.978
CMBO	0.083	3.79	3.98	0.992

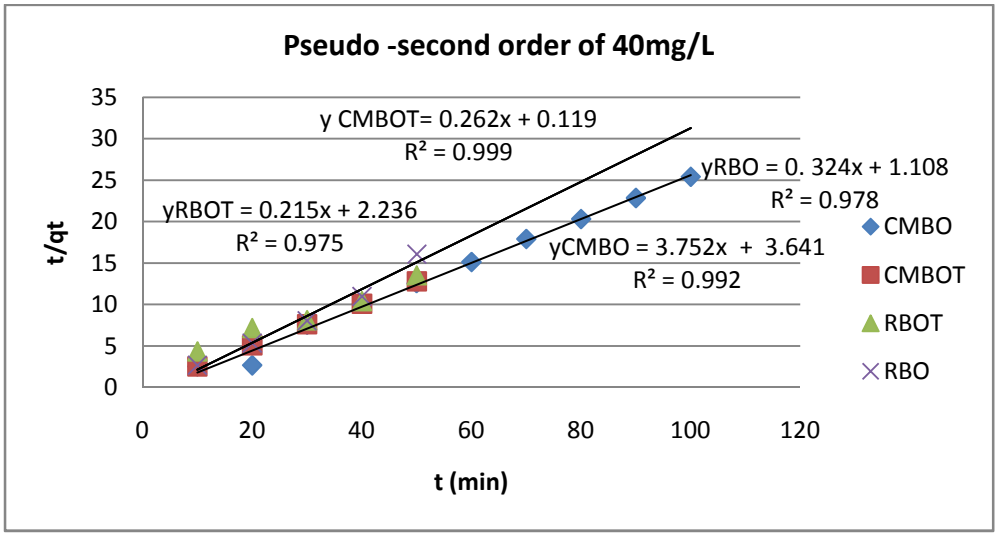


Figure 24 Pseudo-second order kinetic plots for the adsorption of Cr (VI) onto CMBOT, RBOT, RBO and CMBO, Concentration 40mg/L at optimum condition.

4.6. Adsorption Isotherm

4.6.1 Langmuir Adsorption Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. The model assumes maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The linear form of Langmuir isotherm model is described as [66].

$$\frac{Ce}{qe} = \frac{1}{b\,qM} + \frac{Ce}{qm} \quad \text{.....15}$$

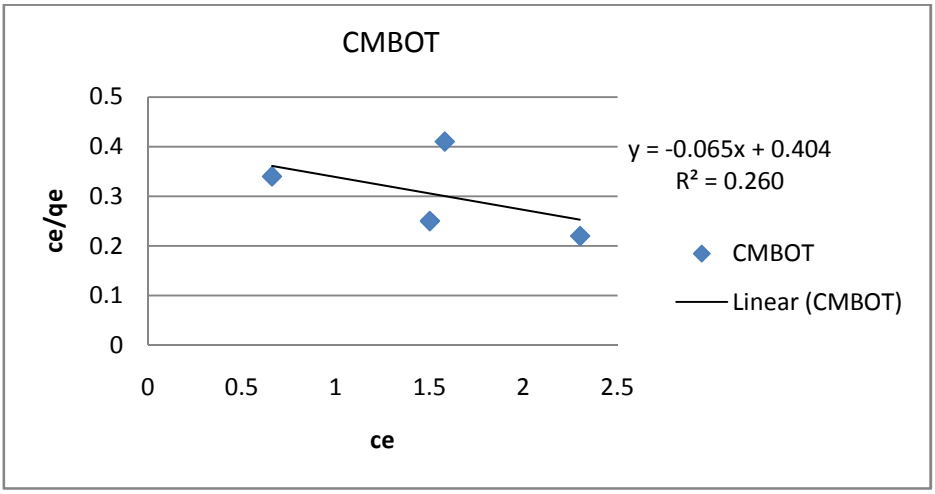
A plot of Ce/qe vs Ce (Figure 25) should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of q_m and b. A further

analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by [94].

$$RL = \frac{1}{1 + bco} \quad \text{.....16}$$

Where: C_0 = initial concentration b = the constant related to the energy of adsorption (Langmuir Constant). RL value indicates the adsorption nature to be either unfavourable if RL >1), linear if RL =1, , irreversible if RL= 0 , and if the average of the *RL* values for each of the different initial concentrations used is between 0 and 1 or 0 < RL < 1, it indicates favourable adsorption [93].

From figure 25a shows the values of Langmuir parameters q_m and b obtained from the slope and intercept of Ce/qe vs. Ce were 15.385 mg/g and 6.22 respectively. Whereas the coefficient of determination (r^2) value was 0.260 which indicates that the data followed the isotherm with poor validity. The value of RL, one of the characteristics of langmuir isotherm was in the range 0.00797 - 0.002 for CMBOT (appendix IV table 1a). This reflects that in all the cases, RL values fall between 0 and 1, indicating favorable adsorption of Cr (VI) and the R^2value is 0.26 proving that the adsorption data poorly fitted to Langmuir Isotherm model.



a)

Figure 25b shows the values of Langmuir parameters q_m and b obtained from the slope and intercept of Ce/qe vs. Ce were 0.619 mg/g and - 0.389 respectively. Whereas the coefficient of determination (r^2) value was 0.761. The value of RL, one of the characteristics of langmuir isotherm was in the range 0.114 - 0.0311 for RBOT (appendix IV table 1a). It was observed that the negative intercept in the graph leads to the value of b and q_m to be negative. Negative values of b and qmax are an indicative of the inadequacy of the isotherm model to explain the adsorption process, since these constants are related to both the surface binding energy and monolayer coverage.

b)

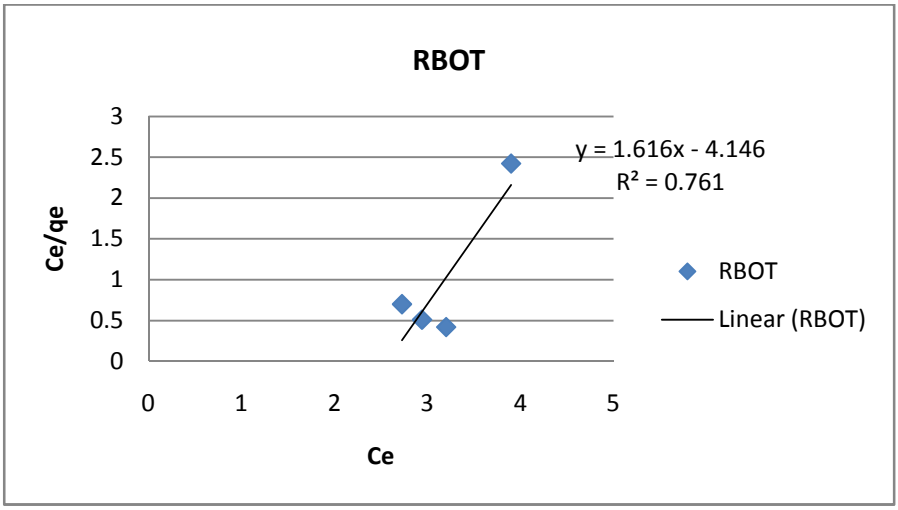
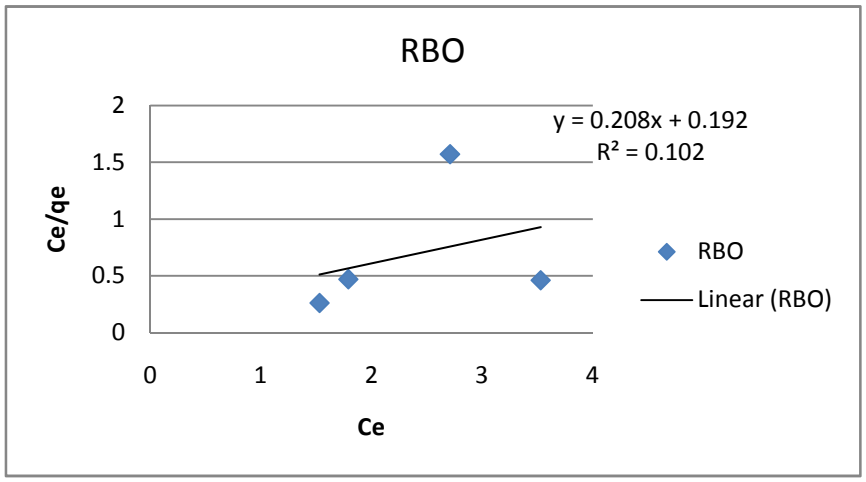


Figure 25c below shows the values of Langmuir parameters q_m and b obtained from the slope and intercept of Ce/qe vs.Ce were 4.81 mg/g and 1.0828 respectively. Whereas the coefficient of determination (R^2) value was 0.102 (appendix IV table 1b). The value of RL, one of the characteristics of langmuir isotherm was in the range 0.0441 - 0.0114 for RBO which reflects the favorability of the adsorption because the value lie between 0 and 1

c)



From figure 25d the values of langmuir parameters q_m and b obtained from the slope and intercept of ce/qe vs.ce were 2.865 mg/g and 6.346 respectively. Whereas the coefficient of determination (r^2) value was 0.818 (appendix IV table 1b). The value of RL, one of the characteristics of langmuir isotherm was in the range 0.00781 - 0.00196 for CMBO. This reflects that in all the cases, RL values fall between 0 and 1, indicating favorable adsorption of Cr (VI). The lower the separation factor the more effective the adsorption. The R^2 value is 0.818 proving that the sorption data fitted well to Langmuir Isotherm model. From the value of correlation coefficients (R^2=0.818) the equilibrium data is better fitted to the

Langmuir isotherm model than the freundlich adsorption model for chemically modified banana and orange adsorbents(CMBO). This implies that all the adsorption site are equivalent and each site can only accommodate one molecule. Further, at the maximum adsorption only a monolayer is formed. Therefore, adsorption only occurs on localized site on the surface, not with the other adsorbate. The surface energetically homogenous and adsorbed molecules do not interact so there is no phase transition.

d)

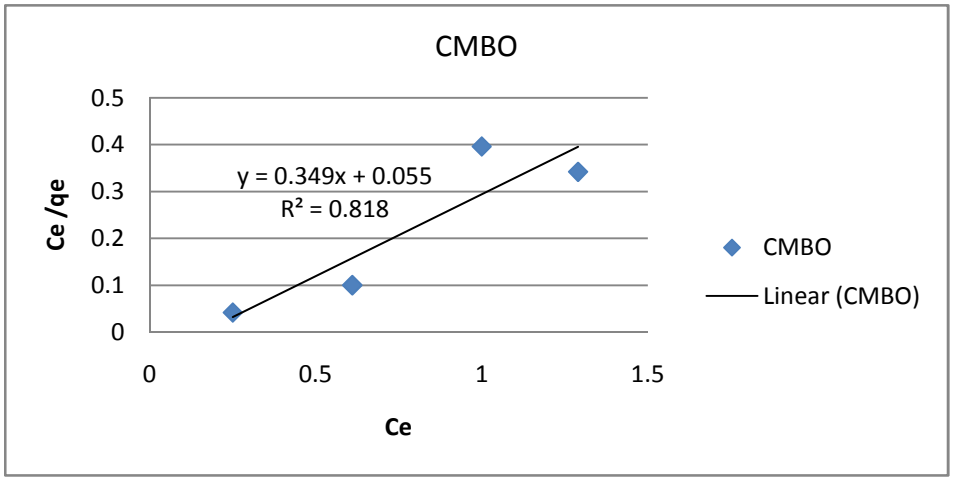


Figure 25 Langmuir isotherm model plots for the adsorption of Cr (VI) onto (a) CMBOT, (b) RBOT, (c) RBO and (d) CMBO

4.6.2. Freundlich Adsorption Isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and is an indicator of the extent of heterogeneity of the adsorbent surface. . Its equation is given as [67].

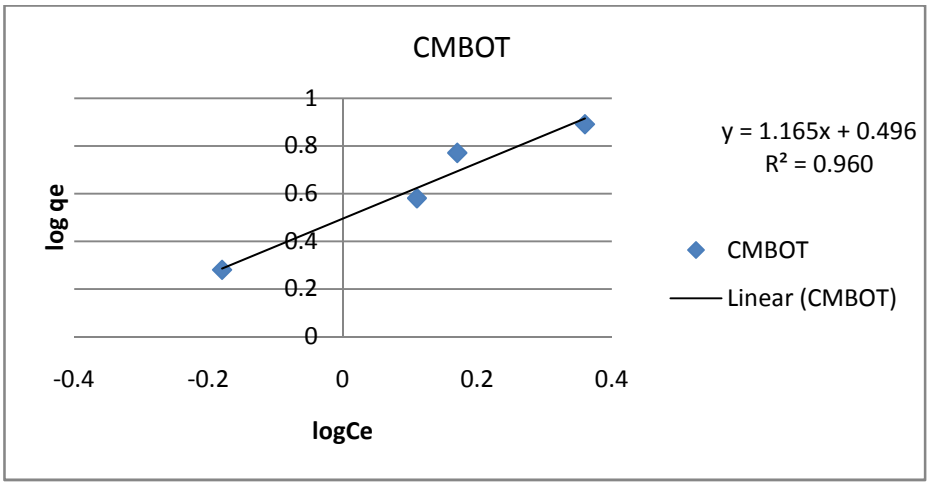
The linear form of Freundlich isotherm is expressed as

$$\text{Log qe} = \text{Log Kf} + \frac{1}{n}\log \text{Ce} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 17$$

Where kf is roughly an indicator of the adsorption capacity and 1/n of the adsorption intensity. kf and 1/n can be determined from the linear plot of log (qe) versus log (Ce) shown in Figure 26 listed the calculated results. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. A relatively slight slope and a small value of 1/ n indicate that, the adsorption is good over entire range of concentration. All tables of freundlich isotherm are listed (summarized) in appendix V, table 1c, 1d, 1e, and 1f.

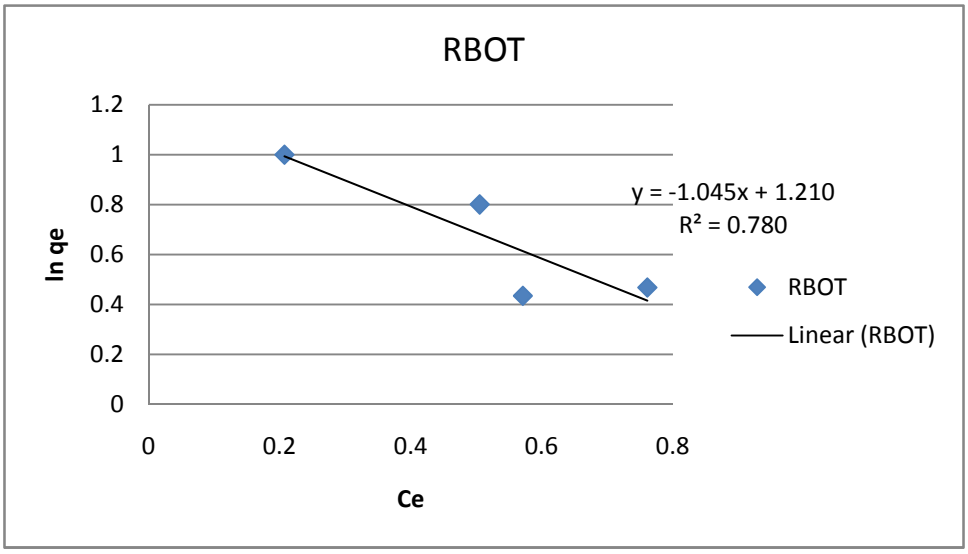
Figure 26a) indicate that the values of freundlich parameters 1/n and Kf obtained from the slope and intercept of the plot logqe vs logCe were 1.165 and 3.133 respectively. The higher value of *Kf* (3.133) indicates the higher adsorption capacity for the CMBOT. Thus also indicating the efficiency of the

phosphoric acid modification process. If n lies in the range 1 - 10, it indicates a favorable sorption process. From the data in Table 1c in the appendix the value of 1/n = 1.165 and hence n = 0.858, indicating that the sorption of Cr(VI) on to CMBOT biomass is cooperative adsorption.



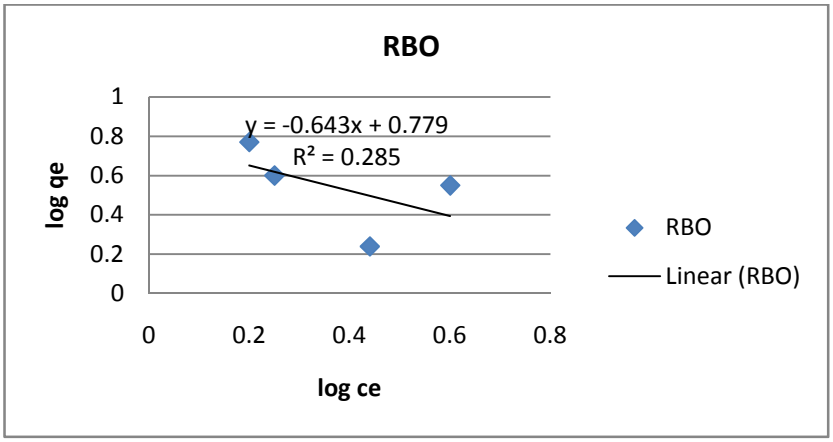
a)

From figure 26b shows the values of freundlich parameters 1/n and Kf obtained from the slope and intercept of the plot loqe vs logCe were -1.045 and 16.23 respectively and confirmed that Cr(VI) removal using RBOT a at pH 2 and 25^{0}C was a favorable adsorption process. Since Kf much greater than qm of Langmuir the adsorption follows freundlich adsorption isotherm i.e 16.23 > 0.619.



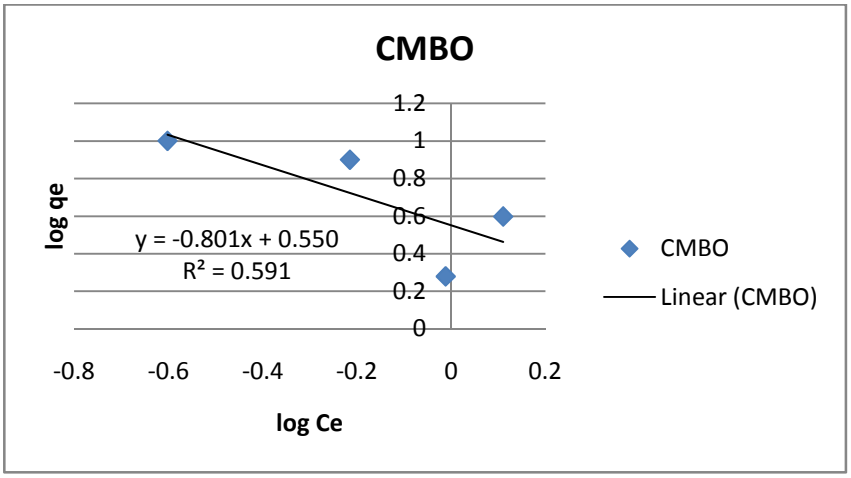
b)

Figure 26c shows value of freundlich parameters 1/n and Kf obtained from the slope and intercept of the plot logqe vs logCe were -0.643 and 6.01 for RBO respectively. It could be inferred that the adsorption follow normal Freundlich isotherm.



c)

From the figure 26d the values of freundlich parameters 1/ n and Kf obtained from the slope and intercept of the plot logqe vs logCe were -0.801 and 3.458 respectively. The R^2 value was found to be 0.591, which indicates that the data followed the isotherm with poor validity. The negative value shows the direction of the fitting area.



d)

Figure 26 Freundlich isotherm model plots for the adsorption of Cr (VI) onto (a) CMBOT, (b) RBOT, (c) RBO and (d) CMBO

According to Foo and Hameed [95] the slope ranges between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below 1 implies chemisorption process where 1/n above 1 is an indicative of cooperative adsorption [96]. The n value in Freundlich equation was found to be -0.957, 0.858, -1.25 and -1.56 for RBOT, CMBOT, CMBO and RBO. Since 1/n<1, this indicates the normal adsorption of chromium (VI) onto CMBO, RBO, and RBOT Peel but cooperative adsorption for CMBOT. All the calculated values are summarized in appendix Table 1, 2, 3, and 4. Generally the regression coefficient (R^2) for Freundlich, Langmuir, a isotherm are found to be 0.960, and 0.818 for CMBOT and CMBO respectively. Thus, the Langmuir adsorption isotherm is the best model for Cr (VI)

adsorption on to the CMBO adsorbent. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto CMBO since the Langmuir equation assumes that the surface is homogenous. Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface. The regression of CMBOT and RBOT was 0.960 and 0.780 respectively. CMBOT and RBOT was best and well fit Freundlich adsorption model.

Comparison of Adsorption Capacity with other Low - cost Adsorbent: The adsorption capacity of Cr(VI) onto CMBOT , CMBO, RBOT and RBO was compared with low cost adsorbent reported in literature and is shown in table 15. The experimental data of the present investigation were compared with the reported values. Results of the investigation revealed that the mixed adsorbents have higher adsorption capacity than simple banana, orange, mango saw dust and neem leave (table 15). The present finding shows that at 60min 99.83%, 96.33% 96.5%, for CMBOT, RBOT and RBO was obtained and at 120min 99.5% for CMBO which is best as compared to other adsorbent listed in Table 15. The difference in adsorption capacity of fruit peel in this report to those previously reported could be due to the type of fruit peel from which fruit peel was obtained and the difference in experimental conditions for the study of adsorption of Cr (VI).

Table 15 Comparison with other types of agricultural waste adsorbent for chromium (VI)

Adsorbent	Element	Equilibrium time	Adsorption capacity	Reference
Orange peel	Cr(VI)	180 min	32%	Vinodhini and Nilanjana, 2009
Orange peel	Cr(VI)	180 min	29.6 %	Mandina *et al.,* 2013
Mango sawdust	Cr(VI)	120	60 %	Vinodhini and Nilanjana, 2009
Neem sawdust	Cr (VI)	60	80 %	,,,,
Banana peel	Cr (VI)	60min	93.5 %	Candelaria *et al*. 2018
Moringa tea leave	Cr(VI)	60 min	99%	Candice et.al 2017
Banana peel	Cr(VI)	10min	95 %	Jamil et. al 2009
CMBOT	Cr (VI)	60 min	99.83%	Present study
CMBO	Cr (VI)	120 min	99.75%	Present study
RBO	Cr (VI)	60 min	96.5%	Present study
RBOT	Cr (VI)	60 min	96.33%	Present study

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The findings in this study revealed that mixed fruit peel can be effectively be employed as an eco-friendly adsorbent for the removal Cr (VI) ions form aqueous solutions. Adsorption efficiencies of mixed fruit peel waste toward the removal of Cr (VI) in aqueous solution were investigated by 250 μm particle size. From the present study, it is concluding that smaller the particle size the larger the surface area and high number of binding site exposed to interact with the metal ions in solution. CMBOT has complete ability to remove the chromium, very little greater than about CMBO. It is more effective and economical as compare to any other combination of biomass. Chromium adsorption on these adsorbents is highly dependent upon solution pH. The optimum pH for CMBOT peel and CMBO peel is found to be 2 with removal efficiencies of 99.83% and 99.75% respectively. The maximum removal of chromium occurs at an adsorbent dosage of 0.5g/ 50mL for, at optimum contact time 60 and 120 min , at room temperature for CMBO and CMBOT respectively.

FTIR analysis was employed the functional group responsible for adsorption of chromium based on the changes in vibration frequencies. The surface morphology and the porosity of the adsorbent were investigated by SEM analysis. The SEM - EDX analysis demonstrates that the metal sorption is highly heterogeneous. The Cr (VI) adsorption is a complex process, in which carboxyl, amino, alcohol group and sulphonic groups are involved. $HCrO_4^-$ species form a series of metal complexes with these groups; the hexavalent chromium ions are simultaneously reduced to trivalent chromium ions by alcohol groups. The newly reduced Cr(III)forms metal-organic complexes via ion exchange and/or coordination reactions. The data obtained in this study was described by Langmuir and Freundlich isotherm. Langmuir and Freundlich isotherm models, with separation factor ($0< R_L <1$) and n values($1/n < 1$) showing favourability for the normal adsorption of chromium. Freundlich isotherm model shows a better agreement with the equilibrium data for CMBOT, RBOT and RBO while CMBO was lamgumiur. Langmuir adsorption isotherm fitted best for CMBO implying that there was monolayer coverage of the metal ions on the surface of the adsorbent, homogenous distribution and that the surface was uniform. The adsorption data also fitted well for pseudo-second-order model. The present investigation clearly indicated that mixed fruit peel are an effective for the removal of chromium from aqueous solution.

5.2 Recommendation

Based on the results of the present study, the following recommendations are suggested for further investigations

- Study can also be performed on industrial waste water of various other industries like tannery and textile industries etc.
- Thermodynamics study can be performed by using both adsorbents (CMBOT peel and CMBO peel) for further investigation.
- A future study is necessary to examine the removal efficiency of chromium on this adsorbent by using comparative study of single and mixed fruit peel adsorbent
- The main objective of this study was to prevent pollution of the environment by chromium. Therefore, chromium loaded chemically mixed banana, orange and turmeric has to be managed by doing desorption experiments to recover chromium from the adsorbent surface.
- The effect of temperature on the removal efficiency should also be studied as adsorption is affected by temperature even keeping other parameters constant.
- Detailed study on disposal of FPW after adsorption needs to be carried out. FPW has some calorific value and can be used in biomass gasification after adsorption

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Annexure

Annex 1. Calculation of Potassium Dichromate Requirement to Prepare 1000 mg/L of Cr(VI) Stock Solution

Calculate how much $K_2Cr_2O_7$ is required to get concentration of Cr (VI) stock solution of 1000mg/L (1g/L). Potassium dichromate ($K_2Cr_2O_7$) has molecular weight = 2*39 + 2*52 + 7*16 = 78 + 104 + 112

= 294 g/mol

104 g Cr (VI) is available in = 294 g of $K_2Cr_2O_7$

1 g Cr (VI) is available in = (294/104)*1 = 2.828 g of $K_2Cr_2O_7$

Annex 2. Calculation of Cr (VI) standard solution

Concentration of stock Cr (VI) solution=1000mg/L. Preparation of Concentration of standard chromium working solution from stock Cr (VI) solution

Initial Cr (VI) C1=1000mg/l (1mg/ml) mass of stock solution= mass of diluted solution

C2 = 10mg/L $C_1V_1=C_2V_2$ V_2=1000mL V1 = C2V2/C1=1000mL*10mg/L/1000mL=10mg/L

Similarly 20,40, 60, 80mg/L was prepared

Table 1 Standard hexavalent chromium calibration curve data

Conc. (mg/L)	Absorbance
0	0
80	2.997
60	2.752
40	1.691
20	0.889
10	0.323

Annex 3. Calculation for the Preparation of 0.1 M NaOH

0.4 g of NaOH pellet was dissolved by distilled water in 100mL volumetric flask

Annex 4 Calculation for the preparation of 0.1M HCl

0.83 mL of concentrated hydrochloric acid was dissolved in 100mL distilled water

Annex 5. Calculation for the Preparation of 6 N H_2SO_4 from 98% stock standard H_2SO_4

Molarity = 10*% of stock H_2SO_4*density / M.wt

M1v1 = m2v2 v1 = m2v2/m1 3 M* 100mL/18M = 16.67 mL

Therefore , take 16.67 mL of sulphuric acid from the stock and dilute to 100mL with distilled water to the mark.

Annex 6.Calculation for the preparation of 85% (w/v) H_3PO_4

85g of H_3PO_4 in 100 mL of water since the density of water is 1g/mL

Density of H_3PO_4 =1.685 g/mL

1ml =1.685g 85 g =?

1.685g/ mL * 0.85 *10 / 98 g/mol= 14.62 M

$M_1V_1 = M_2V_2$ V1 = 0.1 M * 1000 mL / 14.62 = 6.84 mL, Therefore, take 6.84 mL of H_3PO_4 from the stock and dilute to 1000 mL with distilled water to the mark.

Annex 7 preparation of 1,5 Diphenyl carbazide (DPC)

0.25 g of 1,5 diphenyl carbazide (DPC) diluted in 50 mL of acetone. The solution is prepared freshly before use. Store in brown bottle for further use

Appendix

Appendix -I

First order Kinetics data for 60 ppm Cr(VI) for CMBOT, RBOT,CMBO, RBBO

Concentration : 60ppm (CMBOT)						
Time	Mass	Volume	qt(mg/g)	qe(mg/g)	qe- qt	Ln qe-qt
30	0.5	50	5.946	5.99	0.044	-3.129
60	0.5	50	5.99	5.99	0	-
90	0.5	50	5.95	5.99	0.04	-3.22
120	0.5	50	5.95	5.99	0.04	-3.22
Concentration : 60ppm (RBOT)						
Time	Mass	Volume	qt(mg/g)	qe(mg/g)	qe- qt	Ln qe-qt
30	0.5	50	5.696	5.78	0.084	-2.477
60	0.5	50	5.78	5.78	0	-
90	0.5	50	5.57	5.78	0.21	-1.56
120	0.5	50	5.48	5.78	0.3	-1.204
Concentration : 60ppm (CMBO)						
Time	Mass	Volume	qt(mg/g)	qe(mg/g)	qe- qt	Ln qe-qt
30	0.5	50	5.88	5.99	0.11	-2.207
60	0.5	50	5.96	5.99	0.03	-3.51
90	0.5	50	5.984	5.99	0.006	-5.11
120	0.5	50	5.99	5.99	0	
Concentration : 60ppm (RBO)						
Time	Mass	Volume	qt(`mg/g)	qe(mg/g)	qe- qt	Ln qe-qt
30	0.5	50	5.775	5.79	0.015	-4.1997
60	0.5	50	5.79	5.79	0	-
90	0.5	50	5.73	5.79	0.06	-2.8134
120	0.5	50	5.7	5.79	0.09	-2.4079

Appendix II

Second Order Kinetics data for 60 ppm Cr (VI) for CMBO and RBOT

	CMBOT		RBOT		CMBO		RBO	
time	qt(mg/g)	t/qt(mg/g)	qt	t/qt	qt	t/qt	qt	t/qt
30	5.946	5.045	5.696	5.267	5.88	5.105	5.775	5.1948
60	5.99	10.017	5.78	10.3806	5.96	10.068	5.79	10.3625
90	5.95	15.126	5.57	16.158	5.984	15.04	5.73	15.7068
120	5.95	20.168	5.48	21.898	5.99	20.33	5.7	21.0526
150	Not done	Not done	Not done	Not done	5.86	25.597	Not done	Not done

Appendix III

	ln qe-qt(frist order ,40mg/L)				t/qt (second order ,40mg/L)			
Time	CMBO	CMBOT	RBOT	RBO	CMBO	CMBOT	RBOT	RBO
10	-2.99	0.432	-4.1997	-2.21	2.545	2.5316	4.35	2.67
20	-1.386	0.0488	-3.912	-2.23	2.681	5.0697	7.168	5.34
30	-3.51	-2.12	-3.594	-2.21	7.56	7.619	8.1	8.028
40	-3.689			-1.61	10.114	10.088	10.42	10.96
50		-1.966	-4.045		12.563	12.788	13.513	16.06
60	-4.343				15.125			
70	-2.66				17.903			
80	-3.22				20.305			
90	-3.912				22.843			
100	-3.158				25.397			

Appendix IV

Table 1a Langmuir isotherm parameter for CMBOT and RBOT

	CMBOT				RBOT			
Initial Cr (VI) Concentration(mg/L	RL	Qm	b◦	R^2	KL	qm	b◦	R^2
20	0.00797	15.38	6.22	0.26	0.114	0.619	0.389	0.761
40	0.004				0.604			
60	0.00267				0.042			
80	0.002				0.032			

Calculation for Langmuir isotherm parameter (CMBOT) (KL , b_0 and qm)

$Y = 0.065x + 0.404$

$\frac{Ce}{qe} = \frac{1}{b0qm} + \frac{ce}{qm}$ slope = 1/qm , qm = 1/slope , 1/0.065 = 15.38

Y = $\frac{1}{boqm}$ = bo = $\frac{1}{ybo}$ = 1/0.404 x 15.38 = 6.22 then, $RL = \frac{1}{1+bo\ co}$ for 20mg/L

$\frac{1}{1+6.22x20}$ = 0.00797, Similar calculation are followed for RBOT,RBO and CMBO

Table 1b Langmuir isotherm parameter for CMBO and RBO

	CMBO				RBO			
Initial Cr (VI) Concentration(mg/L	RL	qm	b◦	R^2	KL	qm	b◦	R^2
20	0.00781	2.865	6.345	0.818	0.0441	4.807	1.0828	0.102
40	0.00394				0.0225			
60	0.00262				0.015			
80	0.00196				0.0114			

Appendix V

Table 1c Freundlich isotherm parameter(CMBOT)

	Parameter							
Initial Cr (VI) Concentration(mg/L	Ce	qe	Log Ce	Log qe	Ce/qe	Kf	1/n	R^2
20	0.66	1.93	- 0.18	0.28	0.34	3.133	0.858	0.960
40	1.58	3.84	0.11	0.58	0.41			
60	1.5	5.85	0.17	0.77	0.25			
80	2.3	7.77	0.36	0.89	0.22			

Calculation for Freundlich isotherm parameter(CMBOT) (Kf and 1/n)

Y = 1.165x + 0.496

Log qe = log Kf + 1/n logCe

Y = log kf

Slope = 1/n

n = 1/slope

1/1.165 = 0.858

Y = log kf

Kf = e^0.496 = 1.64

Similar calculation is used for RBOT ,RBO and CMBO

Table 2d Freundlich isotherm parameter (RBOT)

		Parameter						
Initial Cr (VI) Concentration(mg/L	Ce	qe	Log Ce	Log qe	Ce/qe	Kf	1/n	R^2
20	3.9	1.61	0.207	1.00	2.422	16.23	0.606	0.780
40	2.725	3.73	0.571	0.435	0.7			
60	2.94	5.77	0.761	0.468	0.51			
80	3.2	6.33	0.5051	0.801	0.42			

Table 3e Freundlich isotherm parameter(RBO)

	Parameter							
Initial Cr (VI) Concentration(mg/L	Ce	qe	Log Ce	Log qe	Ce/qe	Kf	1/n	R^2
20	2.71	1.73	0.44	0.24	1.57	6.01	-1.56	0.285
40	1.79	3.82	0.25	0.6	0.47			
60	1.53	5.85	0.2	0.77	0.261			
80	3.53	7.65	0.6	0.55	0.461			

Table 4f Freundlich isotherm parameter (CMBO)

	Parameter							
Initial Cr (VI) Concentration(mg/L	Ce	qe	Log Ce	Log qe	Ce/qe	Kf	1/n	R^2
20	1	1.92	- 0.0119	0.283	0.396	3.548	0.801	0.591
40	1.29	3.87	0.11	0.59	0.3421			
60	0.25	5.975	- 0.602	1.00	0.0418			
80	0.61	7.939	- 0.215	0.90	0.1			

Appendix VI

The above Figure shows Drying and preparation of powdered adsorbent A. Turmeric B. Banana and C. Orange

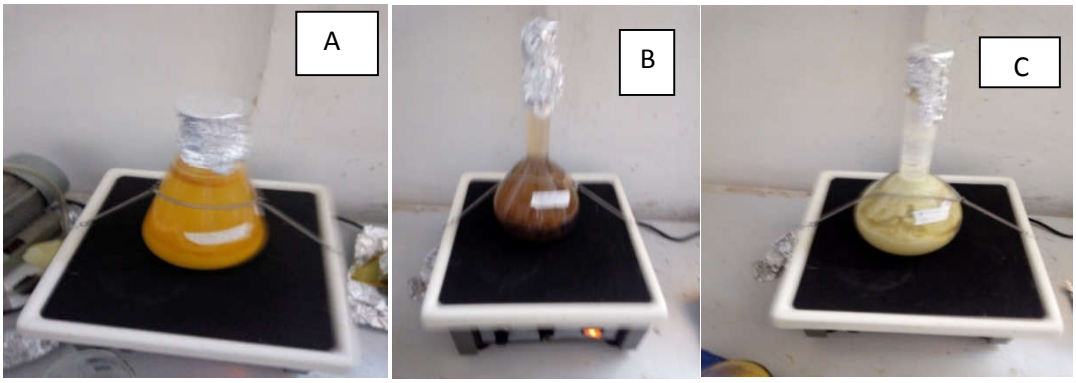

Figure showes Chemical modification of A) BOT mixed adsorbent, B) banana, and C) orange peel using H_3PO_4

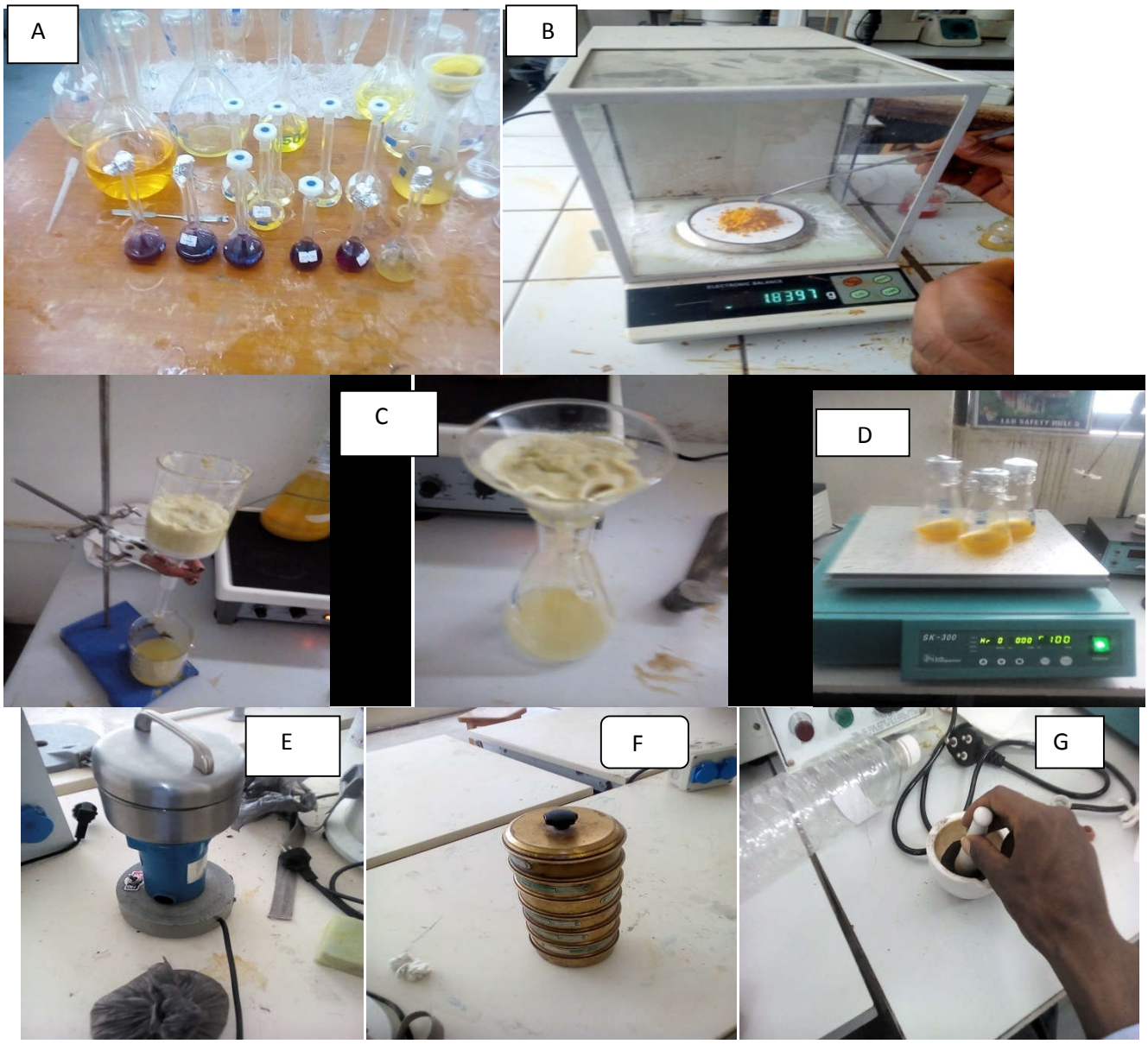

Figure below describe A) stock solution prepared and color development, B) Electronic balance C) filtration funnel for adsorbent filtration D) Electronic Shaker E) Electrical grinding machine F) sieve G) morter and pistel for grinding of H_3PO_4 treated adsorbent.