

**REMOVAL OF CHROMIUM USING
ACTIVATED ALMOND AND APRICOT SHELLS**

*A thesis submitted in partial fulfillment of
The requirements for the degree of*

MASTER OF TECHNOLOGY
In
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by
NEERAJ NIKHIL (2K15/ENE/06)

UNDER THE GUIDANCE OF
DR. ANIL KUMAR HARITASH



**DEPARTMENT OF ENVIRONMENTAL ENGINEERING
DELHI TECHNOLOGICAL UNIVERSITY
(FORMERLY DELHI COLLEGE OF ENGINEERING)**

BAWANA ROAD, DELHI-110042

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DECLARATION

I declare that the work presented in this thesis titled “**removal of chromium using activated almond and apricot shells**”, submitted to Department of Environmental Engineering, is an authentic record of my own work carried out under the supervision of **Dr. Anil Kumar Haritash, Department of Environmental Engineering**, Delhi Technological University, Delhi.

This report does not, to the best of my knowledge, contain part of my work which has been submitted for the award of any other degree either of this university or any other university without proper citation.

Date:

Place: DTU, Delhi

Signature of candidate

CERTIFICATE

DELHI TECHNOLOGICAL UNIVERSITY
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Date:-_____

This is to certify that the report entitled “**removal of chromium using activated almond and apricot shells**” by **Neeraj Nikhil** in the requirement of the partial fulfilment for the award of Degree of **Master of Technology (M.Tech) in Environmental Engineering** at **Delhi Technological University**. This work was completed under my supervision and guidance. He has completed his work with utmost sincerity and diligence. The work embodied in this project has not been submitted for the award of any other degree to the best of my knowledge.

Dr. Anil Kumar Haritash
Assistant Professor,
Department of Environmental Engineering

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(2K15/ENE/06)

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ABSTRACT

Activated carbon was prepared from almond and apricot shells which are a waste material abundantly found. Physical methods were used for activation of almond and apricot shells which involved washing and drying followed by Pyrolyzing in muffle furnace at 450 degree Celsius for two hours and then conversion to a fine powdered form. The various physical and chemical properties of these activated almond and apricot shells were analyzed. The adsorption of hexavalent chromium on activated shells was studied. The adsorption process parameters like pH contact time, adsorbent dose and temperature were optimized.

Keywords: almond shells, apricot shells, optimization, activation

1. INTRODUCTION

Nature has provided plenty of resources that are used to sustain and develop life on the planet. One of the most important resources available to us is water, which was present long before the evolution of life and without which life is not possible. The available water is distributed in an uneven manner, According to a World Health Organization fact sheet and other sources of the total amount of water present on the earth, 97.5% is salt water and cannot be used without treatment. The remaining water (2.5%) is generally fresh but most of it (70%) is locked in polar ice caps and glaciers, and the rest is mostly present as soil moisture or lies in underground aquifers. Overall, the fresh water that is available for use is 1% or 0.007% of the total water on earth, which is really very little. The search for clean, fresh, and potable water has always been one of mankind's priorities. In olden times, when there was no industrial activity, the water available from lakes, rivers and underground reservoirs was pure and suitable for human life. However, with rapid industrialization and modern methods of agricultural and domestic activities, the demand for water has increased tremendously, and this has resulted in the generation of large amounts of wastewater containing a number of pollutants that are harmful to both human and animal life. According to the United Nations World Water Development Report, some 2 million tons of waste per day are disposed of within receiving waters, including industrial wastes and chemicals, human waste, and agricultural wastes (fertilizers, pesticides, and pesticide residues). In addition, according to the World Water Council and the World Health Organization, there is already more wastewater generated and dispersed today than at any other time in the history of our planet, and more than one out of six people lack access to safe drinking water. Also, according to a WHO report, there were an estimated 2.6 billion people in the world without proper sanitation facilities, representing close to 42% of the world's population, and approximately 1.1 billion people did not have access to any type of improved drinking water facility. It is also estimated that by the middle of this century, at worst 7 billion people in sixty countries and at best 2

billion people in forty-eight countries will be water-scarce. The UN policy on sustainable development, established by Agenda 21 and the Rio Declaration on Environment and Development is based on the synergy between economic development, social development, and environmental protection. The use of low-cost adsorbents, particularly if they are based on local natural materials or rural or industrial waste products, for pollution control and management and for securing potable water supplies, can make a significant contribution towards achieving the objectives of Agenda 21 and the Rio Declaration.

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Environmental pollution particularly from heavy metals and minerals in the waste water is the most serious problem in India. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The amount and the number of metals present in any wastewater is related directly to the operations carried out in an industry. For example, tanneries discharge chromium in wastewater; copper, chromium, zinc, and cadmium are widely generated from metal plating; the production of electrical equipment and mining, smelting, and fossil fuel combustion contribute to mercury pollution; and lead is generated from a number of industrial and mining sources. In most wastewaters, the concentration of heavy metals present is much larger than the safe permissible limits and, therefore, they need to be removed. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health. The release of large quantities of hazardous materials into the natural environment has resulted in a number of environmental problems and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health.

2. LITERATURE REVIEW

2.1 Heavy metals toxicity

Heavy metals are those elements having atomic weights between 63.5 and 200.6, and a specific gravity which is greater than 5.0. Most of the heavy metals are dangerous to health and to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya *et al.*, 2003). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers. Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods.

Table 2.1: Sources and toxicological effects of some heavy metals

Heavy metals	Sources	Effects
Copper	Copper water heaters; Water pipes; Frozen greens and canned green making use of copper to produce an ultra green colour, Alcoholic beverages from copper brewery equipment; Instant gas hot water heaters; Hormone pills; insecticides; Pesticides; fungicides;	Arthritis/rheumatoid arthritis; Mental disorder, Anaemia; Hypertension, Nausea/vomiting, Hyperactivity, Insomnia, Autism, Stuttering, Schizophrenia, enlargement

	Cooper cooking pots; Copper jewellery	of liver, heart problem, Cystic fibrosis.
Chromium	Steel and textile industries.	respiratory problems, haemolysis, Skin rashes, acute renal failure, weakened immune systems, alteration of genetic material, kidney and liver damage, lung cancer, Pulmonary fibrosis.
Nickel	Effluents of silver refineries, zinc base casting and storage battery industries, electroplating.	Encephalopathy, pulmonary fibrosis, cancer of lungs, Dermatitis, dizziness, nausea and vomiting, Myocarditis, nose and bone headache, chest pain, rapid respiration.
Lead	Industries such as mining, automobile, steel, batteries and paints. Pollutants arising from the increasing industrialization.	Nausea, Headache and vomiting, Mental retardation, Learning difficulties, Hyperactivity, kidney damage.
Mercury	Industries like oil refining, rubber processing and fertilizer, chloro-alkali, paints, pulp and paper, batteries, drugs, thermometers, dental fillings adhesives, fabric softeners, fluorescent light tubes and high intensity street lamps, pesticides, cosmetic and pharmaceuticals.	Tremors, Birth defects, Loss of hearing or vision, Gingivitis, Kidney damage, Nausea, Chromosome damage, Seizures, Cerebral palsy, Mental retardation, Tooth loss, Hypertonia – muscle rigidity, Blindness and deafness, Minamata disease.

Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption_ can be used to remove these recalcitrant wastes. So far, a number of efficient methods have been developed for heavy metal removal. Fenglian *et al.* (2011) and Rao *et al.* (2011) reviewed various methods for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult. The sludge also needs further disposal. In addition, effluent after such treatment usually has an unacceptably high total dissolved solids. When applied to a dilute metal waste or to lower concentrations of the metal ions, these processes are quite ineffective or not cost-effective and they require high level of expertise; so they are not applied by many end-users. However, most of these methods are very costly and require a high level of expertise; hence they are not applied by many users. For these reasons, the adsorption technology has gained a wider application due to its low cost, simplicity, versatility and robustness. Low cost adsorbents, derived from agricultural by-products and industrial solid wastes can be used to remove recalcitrant wastes from the synthetic wastewaters. This entire process of transformation of these materials into adsorbents for wastewater treatment will help to reduce the economics of waste disposal. The adsorption of these toxic wastes from the industrial wastewaters using the agricultural wastes and industrial by-products has been thoroughly investigated (Basu *et al.*, 2006; Srivastava *et al.*, 2006). The technical suitability of various low-cost adsorbents for the heavy metals removal from waste water has been reviewed (Babel *et al.*,2003).Instead of using the commercial activated carbon, researchers have worked on cheaper and inexpensive materials, such as zeolites, chitosan, and various other adsorbents, which have large adsorption capacity and are locally available.

2.2 Various Conventional Methods of Heavy Metal Removal

2.2.1 Chemical precipitation

Chemical precipitation processes involves addition of the chemical reagents which is followed by the separation of the precipitated solids from the clean water. Precipitation of these heavy metals is achieved by the addition of coagulants such as alum, iron salts, lime and other organic polymers. Gopalratnam *et al.* (1988) found that there is 80% removal of Zinc, Copper and Lead and up to 96.2% removal of oils from industrial wastewaters using a joint hydroxide precipitation and air floatation system.

2.2.2 Electrodialysis

Electrodialysis (ED) is a membrane process, during which the ions are transported through a semi permeable membrane, under the influence of an electric potential. These membranes are cation or anion selective, which means that either positive ions or the negative ions will flow through. Cation-selective membranes are polyelectrolytes with a negatively charged matter, which rejects the negative charged ions and allows only positively charged ions to flow through.

2.2.3 Coagulation/ flocculation

Coagulation and flocculation are very essential part of drinking water treatment as well as for wastewater treatment. Coagulation is the chemical reaction which occurs when a chemical or a coagulant is added to water. The coagulants encourage the colloidal material in the water to combine together into small aggregates called as flocs. The Suspended matter is then attracted on these flocs. Flocculation is the slow gentle mixing of the water which encourages the flocs to form and grow to a size which facilitates easy settlement. Randtke *et al.*(1997) reviewed the basic mechanism involved in removal of the organic contaminants by the coagulation process. Kuo *et al.*(2001) studied the effects of the initial pH and the turbidity, alum and pre ozonation doses, and the impact of flocculation time on the removal of dissolved and colloidal organic matter during coagulation.

2.2.4 Ultra filtration

Ultrafiltration is a separation process which involves membranes with pore size in the range of 0.1 to 0.001 micrometre. Typically, ultrafiltration removes high molecular-weight substances, the colloidal materials and the organic and inorganic polymeric

molecules. This process is a pressure-driven purification process in which the water and other low molecular weight substances permeate through a membrane while the particles, colloids and the macromolecules are retained. The primary removal mechanism in this process is size exclusion, although the electrical charges and the surface chemistry of the particles or membrane may also affect the purification efficiency.

2.2.5 Reverse osmosis

In the reverse osmosis process a cellophane-like membrane separates purified water from the contaminated water. In this process a pressure is applied to the concentrated side of the membrane forcing the purified water into the dilute side with the rejected impurities from the concentrated side being washed away to the reject water. Applications that have been reported for reverse osmosis processes include the treatment of the organic contaminated wastewaters, wastewaters from electroplating and metal finishing industries, pulp and paper industries, mining and petrochemical industries, textile, and food processing industries, radioactive wastewater, municipal wastewater, and the contaminated groundwater (Slater *et al.*, 1983; Cartwright, 1985; Ghabris *et al.*, 1989; Williams *et al.*, 1990).

2.2.6 Adsorption

Adsorption is a process which occur when a gaseous or a liquid solute accumulates on to the surface of a solid or a liquid (adsorbent), forming a very thin molecular or an atomic film (the adsorbate). Adsorption is usually operative in most natural, physical, biological, and chemical systems, and is significantly used in the industrial applications. Adsorption is currently considered to be highly suitable for wastewater treatment because of its simplicity and cost effective approach. (Yadanaparathi *et al.* 2009, Kwon *et al.*, 2010,). Adsorption is one of the commonly used techniques for the removal of the metal ions from several industrial effluents (Gottipati *et al.*, 2012). Activated carbon is the most widely used adsorbent. It is highly porous, amorphous solid which consists of micro crystallites with graphite lattice and is usually prepared in the form of small pellets or powder. It can remove a wide variety of the toxic metals. Some most commonly used adsorbents for adsorption of metal ions include activated carbon (Pollard *et al.*, 1992, Satapathy *et al.*, 2006), clay minerals (Wilson *et al.* 2006), biomaterials, zeolites and industrial solid wastes (Wang *et al.*, 2008). Some Natural materials or certain wastes from

industrial or agricultural operation are one of the sources for the low cost adsorbents. These materials are, generally locally and easily available in large quantities. Therefore, they are cheaper and have less economic value.

2.3 Adsorbents

The most important property that any good adsorbent must possess is a porous structure resulting in very high surface area. In addition, the time taken for the adsorption equilibrium to be established should be as small as possible such that it can be used to remove the contaminants in lesser time. Thus, for the removal of pollutants, one looks to adsorbents with higher surface area and porosity and the one showing fast adsorption kinetics. Some of the important adsorbents which are frequently used in industry and for pollution control are discussed now.

2.3.1 Alumina and bauxite

Alumina is a synthetic porous and crystalline gel, which is available in the granular form in different sizes. It is investigated to have a surface area in the range of 200–300 m²g⁻¹ and is used in industrial applications requiring the removal of water from gas streams, decolorization, and refining of the petroleum oils and waxes. On the other hand, bauxite is naturally occurring, porous crystalline alumina contaminated with varying proportions of kaolinite and iron oxides depending on the place of origin. It is commonly used in the place of alumina, and it has been experimentally found that it removes most of aerobic and anaerobic bacteria. Its surface area ranges from 25 to 250 m²g⁻¹.

2.3.2 Silica gel

It is prepared from the coagulation of colloidal silicic acid, which results in the formation of porous and non crystalline granules of varying sizes. It shows much higher surface area as compared to alumina, which is in the range of 250 to 900 m²g⁻¹. Silica gel is considered a very good adsorbent and is used in several industries for drying of gases and liquids, purifying of hydrocarbons, etc.

2.3.3 Zeolite and ion exchange resin

Zeolites are microporous adsorbents that occur naturally and are also manufactured synthetically. They are also considered to be a selective adsorbent and show ion exchange property as well as the molecular adsorption. Zeolites are crystalline tectosilicates which can undergo reversible base-exchange reactions. Previously Zeolites were formed by fusing calculated amounts of feldspar, clay, and soda ash. Later on, synthetic zeolites were obtained from the mixture of caustic soda, sodium silicate, and bauxite. Natural zeolites generally show less surface area; however, the actual surface area of some of synthetic zeolites can be as high as $700 \text{ m}^2 \text{ g}^{-1}$. The textural classification of zeolites is usually carried out by measuring their surface area, pore volume, and pore size distribution using low temperature N_2 adsorption and by applying various techniques such as X-ray and neutron diffraction, NMR, and scanning electron microscopy. A number of zeolites have been used for removal of pollutants as well.

2.3.4 Activated carbon

Activated carbon is one of the oldest adsorbents known and is usually prepared from source materials, such as coal, coconut shells, lignite, and wood, using one of the two basic activation methods. Activated carbon for the water treatment is available in two major forms: powdered activated carbon (PAC) and the granular activated carbon (GAC). Most of the work on the removal of pollutants from wastewater has been on GAC, because of the fact that the granular form is more suitable to continuous contact, and there is not any need to separate the carbon from the bulk fluid. While on the other hand, the use of PAC presents some serious practical problems as there is a need to separate the adsorbent from the fluid after use. However, in spite of all these problems, PAC is also used for wastewater treatment due to lesser capital cost and lesser contact time requirements.

2.4 Classification:

Activated carbon is quite a complex product and it is very difficult to classify it on the basis of the preparation method, surface characteristics and behaviour. However on the basis of its physical characteristics some general classifications can be made.

2.4.1 Powdered activated carbon:

Traditionally activated carbon is synthesized in particulate form as powder or in form of very fine granules having size smaller than 1.0 mm and average diameter lying in the range of 0.15 to 0.25 mm. In this form the activated carbon present a higher surface area to volume ratio and diffusion distance is very small. Powdered activated carbon constitutes of crushed and finely ground carbon particles such that 97-100% of it passes through specified sieve sizes.

2.4.2 Granular activated carbon:

As per definition granular activated carbon is the one which is retained on 50 mesh sieve. It possesses large particle size in comparison to the powdered activated carbon and therefore has a smaller external surface. For the adsorption process involving gases and vapour granular activated carbon is preferred as diffusion rate is faster in them. Granular activated carbon can be either in granular or extruded form. Notations such as 20×40 are used which signifies that constituting particles will pass through standard mesh size no 20 sieve but will be retained on standard mesh size no 40 sieve. For liquid phase applications sizes generally used are 8×20, 20×40 or 8×30 whereas for vapour phase applications sizes which are employed are 4×6, 4×8 and 4×10.

2.4.3 Extruded activated carbon:

It is basically a combination of powdered activated carbon with a binder such that they are fused together in a cylindrical form. As they possesses high mechanical strength, low dust content and involve low pressure drop.

2.4.4 Impregnated carbon:

Various types of inorganic impregnant as iodine, silver and cations like aluminum, manganese and zinc can be applied on porous carbon. Such impregnated carbon finds special use in air pollution control specially in museums and galleries. Silver loaded activated carbon because of its antimicrobial qualities is utilised as an adsorbent for domestic waste water purification. Adsorption of H₂S and Thiols can also be achieved using impregnated carbon.

2.4.5 Polymer coated carbon:

A biocompatible polymer layer is applied over porous carbon to give smooth and permeable coat without blocking the pores. The product obtained is used for a medical process known as hemoperfusion which is a technique in which in order to remove toxic substances from blood a large volume of patient's blood is passed over the adsorbent substance.

2.4.6 Others:

Activated carbon is also available in certain special forms such as clothes and fibres. For example, carbon cloth is used in personnel protection for the military.

2.5 Properties of activated carbon:

Activated carbon has very high surface area such that a gram of activated carbon possesses area in excess of 500 m^2 . For use in special applications certain other products like carbon aerogels can be used which has even higher surface area, although they are a bit expensive. The high surface area can be examined under an electron microscope. The presence of micropores provides excellent adsorption condition as for adsorbate there is an opportunity to interact with many surfaces simultaneously. Activated carbon uses van der Waals forces or London dispersion forces to bind materials. However certain chemical such as alcohols, glycols, strong acid and bases does not bind well with activated carbon. Activated carbon adsorbs iodine very well and a term iodine number is used as a measure of total surface area.

2.6 Adsorption isotherms

When an adsorbate molecule in the gas phase comes in contact with the surface of the adsorbent, an equilibrium distribution of the adsorbate molecules takes place between the adsorbent surface and the gas phase. This equilibrium distribution depends upon various factors including partial pressure of adsorbate, temperature, nature of adsorbate, and the surface area and nature of adsorbent. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent. Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich. Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature.

2.6.1 Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved.

The linear plot of specific adsorption (C_e/Q_e) against the equilibrium concentration (C_e) shows that the adsorption obeys the Langmuir model.

2.6.2 Freundlich isotherm

The Freundlich isotherm is the most important multisite adsorption isotherm for rough surface. It is a curve relating the concentration of solute on the surface of adsorbent to the concentration of solute in a liquid with which it is in contact. It is empirical in nature. In the Langmuir model, it is assumed that at maximum coverage, there is only a monomolecular layer on the surface. This means that there is no stacking of adsorbed molecules. The Freundlich isotherm does not have this restriction.

A linear plot of $\log(Q_e)$ against $\log(C_e)$ shows that the adsorption obeys Freundlich isotherm model.

2.7 Low cost alternative adsorbent

Activated carbon remains the most widely studied and used adsorbent, and it has been found to adsorb a variety of materials which include metals, dyes, phenols, and a large number of other organic compounds and bio-organisms, and is therefore used for removal of pollutants from wastewaters by adsorption. The design and operation of this process is convenient and can be handled easily, and the operational cost is therefore comparatively low. As a result, cost of the adsorbent, and the additional cost of regeneration when required, can be a major fraction of the overall process costs. Attempts have therefore been made by several research workers in the field of waste management and pollution control to examine for alternative adsorbents that are economical and less costly than activated carbons. The materials that have been studied for this purpose includes both natural materials and wastes and the by products generated from several industries. These materials may be used as such and sometimes after some minor treatment, and are popularly known as low-cost adsorbents (LCAs). It is worthwhile noting here that all

these materials are usually called substitutes for the activated carbon because of their widespread use and especially for their application in wastewater treatment, which is usually done by activated carbons; however, in a broad and clearer way, they are basically a substitute for all the expensive adsorbents. These low-cost alternative adsorbents can be classified in two ways, either on the basis of their availability (i.e., natural materials such as wood, peat, coal, etc.; industrial/agricultural/domestic wastes or the by products such as sludge, fly ash, bagasse, red mud, etc.; and synthesized products) or depending on their nature (i.e., organic and inorganic).

The selection of the most appropriate adsorbents would be based on some important characteristic properties such as: (i) low-cost combined with the satisfactory adsorption properties (capacity, reuse, industrial-scale use *etc.*) and (ii) eco-friendly nature of each adsorbent. It is fundamental to use only those materials which either have lowest impact on the environmental balance or are environmentally-friendly (from abundant natural sources, biodegradable, non-toxic *etc.*).

2.8 Paperworks:

Numerous works have been recently published with primary objective being the study of the removal of different pollutants (either in a gaseous or a liquid medium) using adsorbent materials. Although, the structure and “philosophy” of the adsorbents used are not same during the years. The latter is due to change of the under-removal-pollutants. Different materials have been enquired as possible wastewater adsorbents. Following are some of the paper works and literature which have been reviewed before carrying out this work.

Poots et al. studied wood as an adsorbent for the removal of telon blue. The adsorbent was examined without any pre treatment and was sieved into various size ranges prior to the use. The kinetics of process was found to be dependent on the particle size, being least (<3h) for small particle size (150–250 μm) and most (>6h) for large particle sizes (710–1000 μm). The monolayer coverage of the dye on wood varied from 6.95 to 11.56 mgg^{-1} for particle sizes varying from 710–1000 and 150–250 μm , respectively. It was suggested that because of its economical nature, the wood adsorbent does not needs to be regenerated after use and can be disposed off by burning, and the heat so generated can be used for producing steam. One of the drawbacks according to the author of the study

was large contact period (8 h) and also quite low adsorption capacity of the adsorbent. They further used the same wood as an adsorbent for the removal of another dye (basic), astrazone blue, but for this system they found a lower contact time (2 h) for equilibrium adsorption and a comparatively higher adsorption capacity of 100.1 mgg^{-1} for particles of size 150–250 μm .

Mittal et al investigated natural coal as an adsorbent for the removal of dyes .The coal was not used as an adsorbent as such but was subjected to sulfonation and heated in a water bath. Sorption and desorption of the two basic dyes, rhodamine B and methylene blue, and the acidic dye sandola rhodine was examined. The desorption studies revealed that methylene blue and rhodamine B sorption is not a physisorption, whereas that of sandola rhodine is. Venkata Mohan et al. made use of coal-based sorbents, namely charfines, lignite coal, and bituminous coal, and presented results on the adsorption of color removal of the trisazo direct dye C.I. Direct brown 1:1 by adsorption onto these adsorbents, and made a comparative study of the results with activated carbon (Filtrisorb-400). The coal-based adsorbents were found to achieve equilibrium in a rather short time (60 min) compared to the activated carbon (400 min), which was suggested to be due to the presence of the acidic groups (carboxyl and hydroxyl) present on the coal-based adsorbents and which also lead to a chemisorption mechanism The sorption interaction of direct dye onto the coal-based sorbents followed a first-order irreversible rate equation, indicating a chemisorption mechanism, while on activated carbon, the data fitted a first-order reversible rate equation suggesting physisorption.

Chui et al. utilized crude shrimp chitin packed in several small columns. Shrimp shell wastes from *Penaeus marginatus* were demineralized by the dilute HCl in several small columns to yield shrimp chitin. 96% of the calcium was efficiently removed by this column method without any removal of proteins. Further, it was found that wastewater from electroplating bath rinsing waters having Cu (II) gave better results. The shrimp chitin removed 92–96% Cu (II) from copper pyrophosphate and acid copper bath rinsing water.

Figueiredo et al. investigated squid, sepia pens, and anodonta shells containing chitin as adsorbents for the color removal from textile wastewaters. These materials were studied with and without any chemical treatment, either by demineralization process followed by

deproteination, or only by one of these two steps. It was reported by these authors that the chemical treatment of the materials under investigation has improved their adsorption capacity, which was most probably due to an increase in relative chitin content. However, they suggested that the dye removal was more suited in continuous operation in a packed column mainly because of biodegradation.

Low et al. used biomass of nonliving dried roots of water hyacinth (not subjected to any pretreatment) as an adsorbent for removal of the methylene blue and victoria blue, and the authors found that it displayed a good adsorptive capacity—128.9 and 145.4 mgg⁻¹ for methylene blue and victoria blue, respectively.

McKay et al. studied the adsorption capacity of Fuller's earth for basic and acid blue to be 220 and 120 mg g⁻¹, respectively, and thus proposed the use of adsorbent for the treatment of the textile effluents. The adsorption capability of clay was suggested to be due to a net negative charge on the structure of the fine grained silicate minerals. This negative charge can be neutralized by the adsorption of the positively charged cations, such as heavy metals, dyes, etc. In addition to this, clays also possess large surface areas ranging up to 800 m²g⁻¹, which significantly contributes to their high adsorption capacity.

Namasivayam and Periasamy transformed peanut hull into an adsorbent peanut hull carbon (PHC) by treating it with concentrated sulfuric acid, then carbonizing in presence of air and subjected to further treatment with 1% sodium bicarbonate overnight. Final treated material was used as an adsorbent for the removal of Hg (II) from aqueous solutions. The adsorption conformed to both Freundlich and Langmuir isotherms. The authors observed higher adsorption capacity (109.89 mgg⁻¹) for the bicarbonate treated peanut hull as compared to a commercial granular activated carbon (12.38 mgg⁻¹), which was suggested to be due to very high porosity and the moderate ion exchange capacity of bicarbonate treated peanut hull in comparison to the activated carbon. The same adsorbent (PHC) was also utilised for Cd (II) adsorption, and the authors found that the process conformed better to the Freundlich as compared to the Langmuir model. However, in the case of Pb (II) adsorption on PHC, the process was found to follow the Langmuir model. In all the cases (i.e., Hg (II), Cd (II), and Pb (II)), the adsorption kinetics was found to be up to five times more faster than that found with the commercial granular activated carbon, and the adsorption capacity was nine to thirty two times higher.

Chamarthy et al. made use of peanut shells to prepare adsorbents by heat treatment in presence of phosphoric or citric acid and used it for adsorption of Cd^{+2} , Cu^{+2} , Ni^{+2} , Pb^{+2} , and Zn^{+2} . Their investigation revealed that phosphoric acid-modified shells have adsorbed metal ions in greater quantity compared to the citric acid modified shells. Besides them, the potential of peanut hull pellets to remove metal ions Cu^{+2} , Cd^{+2} , Zn^{+2} , and Pb^{+2} from wastewater and their performance compared to that of the raw peanut hulls and the commercial grade ion-exchange resin has been carried out by Brown et al. as well. A simple cost analysis done by the researchers has shown that the peanut hulls and hull pellets outperform the resins in terms of gram metal removed per unit media cost.

Ferro et al. adopted batch and column adsorption studies of methylene blue and acid blue 25 onto ground hazelnut shells and sawdust of four wood species—namely, walnut, cherry, oak, and pitch-pine so as to explore the potential use of these materials as a low cost adsorbents for dye removal from the dye house effluents. The adsorption kinetics with all the adsorbents was found to fit a second-order rate equation better than the first-order model. In addition to this the equilibrium data agreed well with the Langmuir's model, and very high adsorption capacity was observed for hazelnut shells as compared to wood sawdust for both dyes. The adsorption capacity for methylene blue was even higher (due to the presence of the polar functional groups) than that for activated carbon from the same material because of the fact that thermal activation develops a highly microporous structure, which is not available to large dye molecules and conversely destroys functional groups on the surface that are involved in adsorption mechanism.

Ferro-Garcia et al., examined almond shell, olive stones, and peach stones as adsorbents after activation for removal of Zn^{+2} , Cd^{+2} , and Cu^{+2} from an aqueous solutions which were found to have significant surface areas of 876, 1103, and 1316 m^2g^{-1} , respectively.

Daifullah and Girgis used apricot stone shells after chemical treatment and low activation for removal of substituted phenols, and suggested that the adsorption of phenols on the adsorbents was inversely proportional to their solubility. The wastes of *Araucaria angustifolia* (also named *pinhão*) in its natural form and loaded with Congo red were tested as a low-cost adsorbent for Cu (II) removal from the aqueous solutions. Optimization study was carried out in order to reduce total number of experiments and to

achieve optimum conditions for the batch adsorption procedure. It was found that the *pinhao* wastes combined with Congo red increased the amount of Cu (II) uptake by more than twice using the Langmuir maximum adsorption or more than thrice using the Freundlich maximum capacity. It was also suggested that the presence of amino and azo groups on the congo red, which is loaded on *pinhao* wastes, is responsible for the enhancement in adsorption capacity,

Sun and Shi explored the possibility of utilizing sunflower stalks, a renewable agricultural waste available cheaply. The source material was subjected to sieving, and adsorption of Cu^{+2} , Zn^{+2} , Cd^{+2} and Cr^{+3} was examined. The adsorption was found to be physical with a capacity of 29.3, 30.73, 42.18, and 25.07 mgg^{-1} for Cu^{+2} , Zn^{+2} , Cd^{+2} , and Cr^{+3} , respectively. Sunflower stalks were also investigated as adsorbents for the basic and direct dyes in aqueous solutions with equilibrium isotherms and kinetic adsorptions. The authors observed very high adsorption capacities for basic dyes in comparison to direct dyes. The authors also suggested that because sunflower stalks consists of cellulose, it is the polyol structure of the cellulose-based materials that causes relatively strong chemical adsorption of cations such as the metal ions and organic bases as well as the physical adsorption of other types of materials such as acidic and anionic compounds. Also, the greater affinity of basic dyes for sunflower stalks than that of anionic dyes can be significantly attributed to cellulosic structure of the materials. The electrostatic forces between the dye species and the negatively charged cellulose in water are major interactions which affect the adsorption of these dyes on the material.

El-Geundi analysed maize cob, an agricultural waste, without any sort of pre-treatment for removal of two basic dyes (astrazone blue and maxilon red) and two acid dyes (telon blue and erinoyl red). This agricultural waste was found to have very high adsorption capacity of 160 and 94.5 mgg^{-1} for astrozone blue and maxilon red and low capacity of 47.7 and 41.4 mgg^{-1} for erinoyl red and telon blue, respectively.

Acemiolu et al. studied use of lignin as an adsorbent for the removal of copper (II). It was investigated that organosolv lignin, which is produced from the delignification of wood and other lingo cellulosics in the organic solvents such as methanol, butanol, and ethanol, have been found to be quite similar to natural lignin but more attractive as it does not

contains sulfur. However, the adsorption of Cu (II) was found to increase largely with concentration and pH and decrease with temperature.

Batzias and Sidiras investigated the potential of a beech saw dust as a low-cost adsorbent, for removal of methylene blue and basic red 22. The authors also examined the potential of the adsorbent on treating it with CaCl_2 and using mild acid hydrolysis, and found it to have an increase in the adsorption capacity. In addition, the simulation studies for the effect of pH were also carried out by authors to determine the point of zero charge p.z.c. (5.2) of the sawdust and suggested that an increase in the pH increases the adsorption behaviour. The lower adsorption of the methylene blue at acidic pH can be attributed to the presence of excess H^+ ions that compete with dye cation for adsorption sites. With the increase in the pH of the system, number of positively charged sites decreases while number of the negatively charged sites increases. It was also found that the negatively charged sites favoured the adsorption of dye (cationic like methylene blue) due to the electrostatic attraction.

Perineau et al. studied wool carbonizing wastes, obtained as a result of processing of wool for the adsorption of dyes. They found that the surface properties of the material are such that it tends to adsorb all solutes of ionic nature. They further concluded that adsorption of basic dyes is 6–10 times higher than those of acid dyes.

Rengaraj et al. attempted to develop an activated carbon from rubber seed coat for removal of phenols using the batch and column operations. They suggested that the adsorbed phenol can be desorbed using sodium hydroxide. The adsorption process was found to obey first-order kinetics and the isotherm was found to fit the Freundlich equation.

Rao et al. investigated raw bagasse which is a waste product from sugar mills and has been used as a low-cost adsorbent for the removal of metals like chromium and nickel from the aqueous solution. They examined the effect of hydrogen ion concentration, contact period, adsorbent dose, initial concentration of adsorbate and adsorbent and particle sizes in batch experiments. The efficiency of the material for removal of Cr (VI) at pH 6 and Ni (II) at pH 8, with a adsorbate concentration 100 mg/L, contact period 90 min, adsorbent particle size 75 μm , and adsorbent dose of 3.5g/L, was found to be 91%

and 85.6%, respectively. The efficiency of bagasse was suggested to be quite comparable to costlier conventional powdered activated carbon.

Isa et al. analysed the scope of using palm oil ash as a low-cost adsorbent for removal of the dyes disperse blue and disperse red from aqueous solution. Both batch as well as continuous flow experiments were carried out, and the effect of different system variables, including that of pH, initial dye concentration, and agitation period, were studied in the batch tests. It was found that acidic pH favoured dye removal, and the optimum pH and agitation period for the removal of two dyes were found to be 2 and 60 min, respectively. In addition, the authors also found that the ash can be used in its natural form in the batch processes, while pelletisation, due to its cost implications, is not recommendable for the industrial applications.

3. OBJECTIVES

The major objectives of this study are:

- Physical activation of almond and apricot shells which are abundantly found as a waste material.
- Characterization of the activated almond and apricot shells and study of their various physical and chemical properties.
- The use of these activated shells for removal of hexavalent chromium from water and optimization of various adsorption parameters like pH, temperature, adsorbent dose and contact period.

4. Materials and methods

The capability of the charcoal to remove odour and taste has been recorded centuries ago. Several literatures show that as per Sanskrit manuscripts from circa 200 BC, “it is good to keep water in copper vessels, to expose it in sunlight and to filter it through charcoal. Activated carbon is the one of the oldest adsorbent that has been known and is usually synthesized from material, like coal, coconut shells, lignite, and wood.

Activated carbon refers to that form of carbon which has been subjected to several processes and treatment in order to increase its porosity and to enhance its surface area. As activated carbons possess high degree of micro porosity just 1 gram of activated carbon has been found to have a surface area as large as 500 m². Generally high surface area directly gives sufficient activation for useful applications, however if subjected to further chemical treatment it generally improves the adsorbing properties.

4.1 Preparation of activated carbon

Activated carbon is the carbon produced from materials with carbonaceous source which include nutshell, almond shells, wood coal and lignite. It may be generated using any of the methods given below.

(a) *Physical activation.* In this process activated carbon is developed from precursor using gases. The treatment to which precursor is subjected to is carbonization which is followed by activation or using either of the two processes. In the first stage of carbonization precursor is Pyrolyzed in an inert atmosphere (nitrogen, argon) and temperature lying in the range of 600–900°C resulting in char formation, which is usually non-porous. In the process of activation the material is exposed to an oxidizing atmospheres (which may be of carbon dioxide, oxygen, or steam) usually in the temperature lying in the range of 600–

1200°C, which leads to the removal of the large portion of disorganized carbon and the synthesis of a well-developed porous structure, leading to very high surface area.

(b) *Chemical activation*. It is one of the other techniques used for the generation of activated carbons and involves use of chemicals like H₃PO₄, KOH, or NaOH, succeeded by heating under a gas (usually nitrogen) flow with the temperature lying in the range of 450 to 900°C. It is of the belief that the carbonization and activation steps occurs at the same time in the chemical activation process. Generally, chemical activation has an advantage over physical activation as it involves less temperature and much shorter time is needed for activating the material.

The product formed by any of the two methods is known as activated carbon and generally has a highly porous structure with surface area lying in the range of 500 to 2000 m²g⁻¹. It has been found that the mechanism of adsorption on activated carbon is not usually a selective one, as it involves van der Waals forces.

4.2 Raw materials:

Almond and apricot are the important stone fruits grown in India. Its main producers are the hilly and Himalayan states of Himachal Pradesh, Jammu and Kashmir and Uttarakhand. It has been found that more than thousands of tonnes of almond and apricot shells are being generated annually. However these shells are waste product as of now and do not possess any commercial value. An uphill task that is being faced by such industries is the management of large amount of almond and apricot shells that is being produced on a daily basis. These shells are waste materials and can be collected for reuse. Activation of these shells can significantly reduce the amount of waste produced in the industrial applications

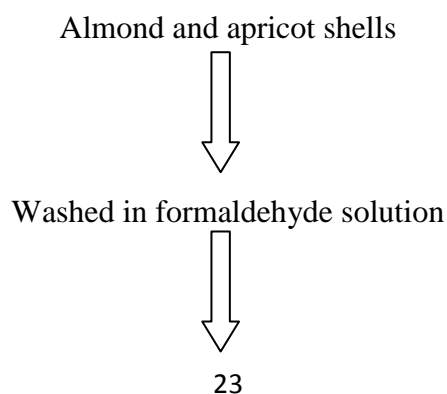
Almond and apricot nutshells are abundant, inexpensive and readily available lignocellulosic material. In the present study these nutshells were used to prepare the activated carbon for the removal of chromium. Alomd and apricot shells were obtained from local market . The present work describes the physical activation process for the manufacturing of activated carbon. Its physical and chemical properties were determined by standard methods.

4.3 Adsorbent preparation:

The various operations involved in the adsorbent preparation are as given below:

- Selection of precursor: Almond and Apricot shells were taken for adsorbent preparation. While selecting the raw materials involved proper care is taken such that the shells should be relatively clean and should not be coated with heavy dirt and mud.
- Washing: The shells are washed with water properly to remove any objectionable materials from them. They are further washed in a formaldehyde solution to remove any colour that may be present in the almond and apricot shells.
- Oven drying: Washed almond and apricot shells are kept in an oven at a temperature of 105°C to remove the moisture present in the shells. After 24 hours they are additionally subjected to a temperature of 180°C for 2 hours to remove any extra moisture if any and to make them suitable for the next operation of pyrolysis.
- Pyrolysis: The dried shells are Pyrolyzed in muffle furnace at 450°C for two hours with the air vents being closed so as to convert them in a char form.
- Disintegration, washing and drying: The charred product obtained after pyrolysis is disintegrated using pestle mortar, is subjected to washing and is further dried. The product so obtained is converted to fine powdered form using mixer.

A flow chart describing entire process of adsorbent preparation is given below.



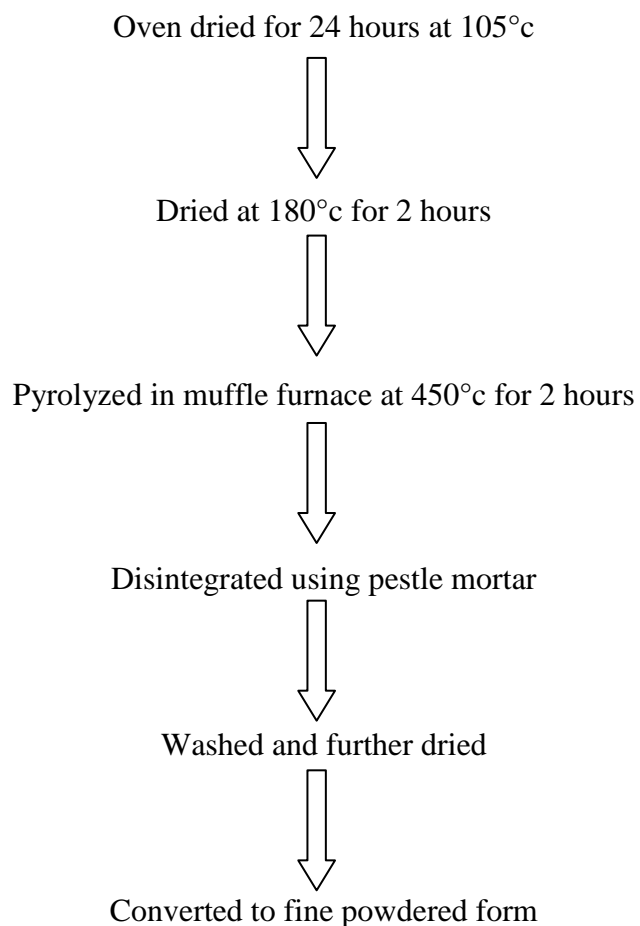


Fig. 4.1: Flow chart for adsorbent preparation

4.4. Preparation of solutions:

All analytical grade reagents were used. Chromium solution was prepared using dissolution of potassium dichromate in distilled water as per standard methods.

5. Characterization of activated samples

This section deals with characterization of activated almond and apricot shells. Characterization of the activated shells is very important in order to analyze not only the important properties of the shells but also to understand how these all properties are going to influence the removal of chromium in the coming sections.

Activated shells which have been prepared in this case proved to be acidic one. Various factors which influence the acidic or basic nature of activated shells can be the steps involved in the preparation of the shells, the presence of chemically active oxygen group on the surface, presence of inorganic matter and the treatment to which the activated carbon has undergone. The various important properties of activated carbon can be classified in two categories i.e. physical and chemical properties.

Some of the important properties which were analyzed are as following:

5.1 pH:

It is a very important property for the activated shells. pH is the measure of hydrogen ions present in the sample. Mathematically it is defined as

$$\text{pH} = -\log_{10}[\text{H}^+]$$

Where H^+ is the concentration of hydrogen ions in moles/litre.

pH of the shells was determined using a properly calibrated pH meter. For the pH determination powdered activated shells were taken and added to water in a beaker. This suspension of the shells in water was then placed in a shaker and was subjected to rotation for 15 minutes at the rate of 150 rpm. After 15 minutes the beaker was removed from the shaker and the supernatant was carefully drained to obtain relatively clear mix, free from powdered shells which was then analyzed using a pH meter.

Table 5.1: pH of the activated samples

Adsorbent	pH
Activated almond shells	4.93
Activated apricot shells	5.20

5.2 Electrical conductivity:

Electrical conductivity is defined as the ability of water to conduct electricity. It gives the concentration of major ions present in water. It is also known as specific conductance and is a function of its ionic strength. This property of electrical conductivity can be determined using a di ionic tester. However it has to be realized that only those substances which can undergo ionisation contributes to specific conductance. Temperature here plays an important role and specific conductance is found to increase with an increase in water temperature.

In order to determine the specific conductance of the activated shells the suspension was prepared in similar manner as during the pH determination and was subjected to shaking for 15 minutes at 150 rpm. The supernatant was drained off to get the clear suspension and it as tested using di ionic tester. The following table lists the value of electrical conductivity of the activated shells.

Table 5.2: Electrical conductivity of the activated samples

Adsorbent	Electrical conductivity (micro mho/cm)
Activated almond shells	195.90
Activated apricot shells	173.20

5.3 Bulk density:

Bulk density of an adsorbent is a very important parameter. It signifies the amount of adsorbent that can be placed in a filter of given solid capacity. Theoretically density is defined as mass per unit volume and the unit is kg/m^3 .

In order to determine the density adsorbent is taken in a 10ml graduated cylinder and is subjected to tamping with rubber pad in the cylinder. This process is continued for 5 minutes such that there is no additional settling produced. The final volume is noted and apparent density is calculated.

For almond shells:

$$\text{Mass measured} = 2.45 \text{ gram}$$

$$\text{Final volume} = 5 \text{ ml}$$

$$\text{Density} = 2.45/5 = 0.49\text{gm/ml}$$

For apricot shells:

$$\text{Mass measured} = 2.05 \text{ gram}$$

Final volume = 5 ml

Density = $2.05/5 = 0.41$ gm/ml

Table 5.3: Bulk density of activated almond and apricot shells

Adsorbent	Bulk density (gm/ml)
Activated almond shells	0.49
Activated apricot shells	0.41

5.4 Yield:

It is an important parameter which signifies the amount of activated products which can be synthesized from a given raw material. This parameter is of quite significance as the steps involved in activation of natural materials is complex so only those raw materials should be activated which give significant yield.

In order to determine the yield of almond and apricot shells a known weight of oven dried shells is taken in a crucible and is then subjected to pyrolysis at 450°C in muffle furnace for two hours to convert them in charred form. The residue is then weighed again to note the final weight.

For almond shells:

Weight of crucible = 71.7453gm

Weight of crucible and dried almond shells = 113.1638gm

⇒ Initial weight of almond shells = $113.1638 - 71.7453 = 41.418$ gm

Final weight after conversion = 16.15302 gm

⇒ Percentage yield = $\frac{16.15302}{41.418} \times 100 = 39\%$

For apricot shells:

Weight of crucible = 71.7453gm

Weight of crucible and dried apricot shells = 109.3042gm

⇒ Initial weight of apricot shells = $109.3042 - 71.7453 = 37.5589$ gm

Final weight after conversion = 12.77002gm

⇒ Percentage yield = $\frac{12.7702}{37.5589} \times 100 = 34\%$

Table 5.4: Percentage yield

Adsorbent	Yield (%)
Activated almond shells	39
Activated apricot shells	34

5.5 Moisture content:

The moisture content of the activated almond and apricot shell is a parameter that signifies the amount of hygroscopic moisture present on the shells. In order to determine the moisture content certain amount of the activated samples were weighed accurately. These samples were then placed in an oven at a temperature for 105°C for three hours. After three hours the samples were removed from the oven and were allowed to cool again in the absence of humidity. These cooled samples were then weighed again. Water content is defined as the difference between the initial and the final mass of activated shells.

For almond shells:

$$\text{Initial weight of crucible} = 71.7453\text{gm}$$

$$\text{Weight of crucible and activated almond shells} = 80.5492\text{gm}$$

$$\Rightarrow \text{Initial weight of activated shells} = 8.8039\text{gm}$$

$$\text{Final weight of oven dried activated shells} = 8.0115\text{gm}$$

$$\Rightarrow \text{Moisture content} = 8.8039 - 8.0115 = 0.7924\text{gm}$$

$$\text{Percentage moisture content} = \frac{0.7924}{8.8039} \times 100 = 9\%$$

For apricot shells:

$$\text{Initial weight of crucible} = 71.7453\text{gm}$$

$$\text{Weight of crucible and activated apricot shells} = 79.4634\text{gm}$$

$$\Rightarrow \text{Initial weight of activated shells} = 7.7181\text{gm}$$

$$\text{Final weight of oven dried activated shells} = 6.8691\text{gm}$$

$$\Rightarrow \text{Moisture content} = 7.7181 - 6.8691 = 0.849\text{gm}$$

$$\text{Percentage moisture content} = \frac{0.849}{7.7181} \times 100 = 11\%$$

Table 5.5: Percentage moisture content

Adsorbent	Moisture content (%)
Activated almond shells	9
Activated apricot shells	11

5.6 Ash content:

Ash content in the activated shells is a measure of the volatile solids present in the samples. In order to determine the ash content the activated samples were burned in

muffle furnace at a temperature of 700°C. One gram of dry, charred activated almond and apricot shells was placed in the crucible and was burned in furnace for four hours. Ash content per gram is defined as the difference between the initial and final weight of the activated samples.

For almond shells:

Initial weight of the activated sample = 1 gm

Final weight of the activated sample = 0.968 gm

Ash content per gram = 1 - 0.968 = 0.032 gm

Percentage ash content = $\frac{0.032}{1} \times 100 = 3.2\%$

For apricot shells:

Initial weight of the activated sample = 1 gm

Final weight of the activated sample = 0.963 gm

Ash content per gram = 1 - 0.963 = 0.037 gm

Percentage ash content = $\frac{0.037}{1} \times 100 = 3.7\%$

Table 5.6: Ash content

Adsorbent	Ash content (%)
Activated almond shells	3.2
Activated apricot shells	3.7

5.7 Iodine value of the activated almond and apricot shells:

The structure of activated carbon is quite complex. In order to have an idea of the porous structure of the activated almond and apricot shells liquid phase iodine adsorption has been adopted. A quick and simple test to determine the surface area of the activated shells with pore size greater than 1 nm, is the adsorption of aqueous I₂. The total quantity of iodine that can be adsorbed per gram of activated almond and apricot shells at an equilibrium concentration of 0.02 N is defined as the iodine value. The tests to determine the iodine number were conducted as per the guidelines laid by American society of testing and materials (ASTM 2006). Mean experimental values are presented.

Iodine number is used as the most basic parameter in order to characterize the activated almond and apricot shells. Iodine number basically represents the acidity level (a higher iodine number signifies that higher degree of activation has been done). It gives a measure of micropore (0-20 Å) content.

Chemicals and reagents which are required in the determination of iodine number are:

- 0.1 N solution of iodine: 40 gm of potassium iodide is taken in a 500 ml and 100 ml of distilled water is added. When solution attains room temperature 12.7 gm of resublimed iodine is added and is subjected to shaking such that iodine dissolves completely. This solution is transferred to the volumetric flask with addition of 3 drops of hydrochloric acid and is further diluted to 1 litre by addition of distilled water.
- 0.05 N solution of sodium thiosulphate: dissolve 12.5 gm of $\text{Na}_2\text{S}_2\text{O}_3$ in 1 litre of distilled water.
- 1 percent starch solution
- Activated almond and apricot shells.

Procedure for iodine number determination

- 10 ml of 0.1 N iodine solutions is taken in the conical flask.
- Add 2 drops of starch solution to it.
- Addition of starch solution turns the pale yellow color of iodine to blue.
- The solution obtained above is titrated with 0.05 N sodium thiosulphate till the time its color is lost and it becomes colorless.
- Burette reading for the above titration is noted say B.
- Accurately weigh 0.2gm of activated almond and apricot shells.
- Place it in a completely dry iodine flask.
- Add 40 ml of 0.1 N iodine solutions.
- Shake the flask properly for 4 minutes and then filter it.
- The filtrate thus obtained is collected in a dry flask and 10 ml of it is titrated against the sodium thiosulphate using starch indicator.
- Burette reading corresponding to the above titration is noted say A.

Calculations:

Iodine number = $C \times$ conversion factor; mg/gm

Where, $C = A - B$

$$\text{Conversion factor} = \frac{\text{molecular weight of iodine} \times \text{normlity of iodine} \times 40}{\text{weig ht of carbon} \times \text{blank reading}}$$

Iodine number calculations for activated almond shells:

$$B \text{ value} = 16 \text{ ml}$$

$$A \text{ value} = 21.5 \text{ ml}$$

$$C \text{ value} = 5.5 \text{ ml}$$

$$\begin{aligned} \text{Conversion factor} &= \frac{\text{molecular weight of iodine} \times \text{normlity of iodine} \times 40}{\text{weight of carbon} \times \text{blank reading}} \\ &= \frac{127 \times 0.1 \times 40}{0.2 \times 16} \\ &= 158.75 \end{aligned}$$

$$\begin{aligned} \text{Iodine number} &= C \times \text{conversion factor} \\ &= 5.5 \times 158.75 \\ &= 873.125 \end{aligned}$$

Iodine number calculations for activated apricot shells:

$$B \text{ value} = 16 \text{ ml}$$

$$A \text{ value} = 17.5 \text{ ml}$$

$$C \text{ value} = 1.5 \text{ ml}$$

$$\begin{aligned} \text{Conversion factor} &= \frac{\text{molecula r weight of iodine} \times \text{normlity of iodine} \times 40}{\text{weight of carbon} \times \text{blank reading}} \\ &= \frac{127 \times 0.1 \times 40}{0.2 \times 16} \\ &= 158.75 \end{aligned}$$

$$\begin{aligned} \text{Iodine number} &= C \times \text{conversion factor} \\ &= 1.5 \times 158.75 \\ &= 238.125 \end{aligned}$$

Table 5.7: Iodine number for activated samples

Adsorbent	Iodine number
Activated almond shells	873.125
Activated apricot shells	238.125

5.8 Methylene blue number of activated almond and apricot shells

Methylene blue number of activated shells gives an idea about its color adsorbing ability. It is used to analyze the presence of micro porosity and meso porosity. In order to determine Methylene blue number activated almond and apricot shells were placed in equilibrium with Methylene blue solution having a concentration of 1.0 mg/l. The amount

of Methylene blue in milligrams which is adsorbed by one gram of activated carbon is reported as Methylene blue number.

In the present the prepared activated almond and apricot shells were tested as per experimental procedures however the activated samples did not show any decolourizing property.

5.9 pH at zero charge:

Acidic or basic character of the surface decides the surface chemistry of any material. It is known that acidic characterizes positive surface charge and basic characterizes a negative surface charge. It is of utmost importance to have information about the surface charge of the material in a aqueous medium, especially in adsorption studies as there may be cases when surface area of the adsorbent material is high but the surface charge on the material is creating a hindrance in adsorption as the nature of surface charge of the adsorbent is same as that of the adsorbate. There is also a need to evaluate the pH corresponding to which the surface charge on the material is zero in aqueous medium or pH_{pzc} (pH point at zero charge).

Procedure for determination of pH_{pzc}:

- A 0.01M solution of NaCl is prepared.
- 50 ml of the solution is taken and is boiled to remove the dissolved CO₂ and is then placed in an air tight system so that the initial pH value is stabilised.
- The pH of the solution of sodium chloride is adjusted to 2 using sodium hydroxide or hydrochloric acid.
- 150 mg of activated almond and apricot shells is added to 50 ml of the NaCl solution that has been adjusted to pH 2 and is then subjected to shaking for 24 hours in an airtight condition with temperature maintained at 25 degree Celsius and speed of 200rpm
- In a similar manner initial pH of 4, 6,8,10 and 12 is attained and is then added with 150 mg of activated almond and apricot shells. These mixes are also placed in air tight condition and are subjected to shaking at 200 rpm for 24 hours.
- After 24 hours of shaking filtration is done and final pH value is measured for each set.

- Final pH is plotted on y axis and initial pH is plotted on x axis
- A line is drawn where the initial pH is equal to final pH.
- pHpzc is basically a point where transition of surface charge of adsorbent material occurs. So the point where initial pH line cuts the final pH line will be the pHpzc value for the activated shells.

pHpzc calculations for activated almond shells:

Activated almond shells were subjected to treatment as specified above and the initial pH and final pH were obtained.

Table 5.8: pHpzc for activated almond shells

Initial pH	Final Ph
2	4.30
4	4.89
6	6.14
8	7.2
10	8.4
12	10

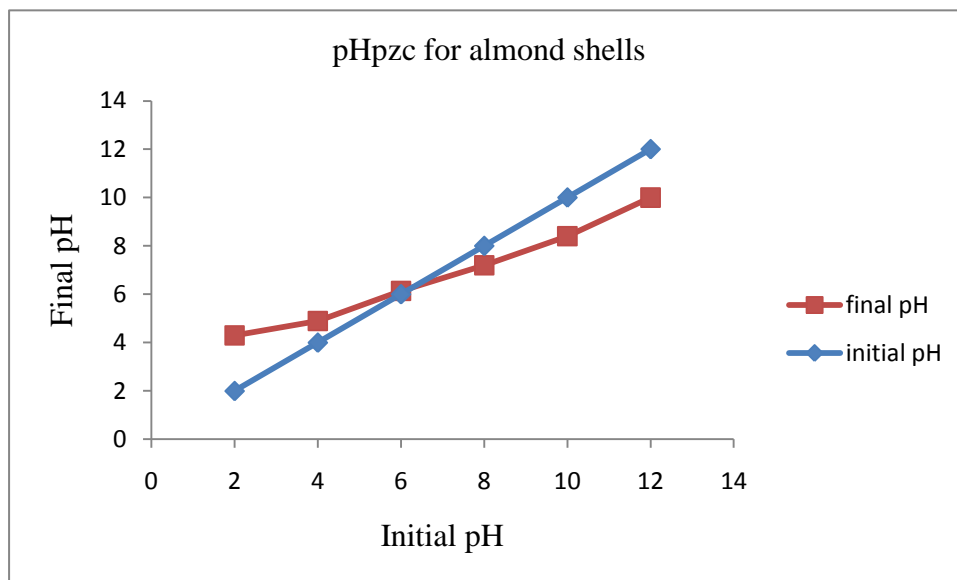


Fig. 5.1: pHpzc for activated almond shells

As it can be seen from the curve that initial pH line cuts the final pH line at a pH value which is around 6. So pH_{pzc} for the activated almond shells is 6.

pH_{pzc} calculations for the apricot shells:

Activated apricot shells were subjected to treatment as specified above and the initial pH and final pH were obtained.

Table 5.9: pH_{pzc} for activated apricot shells

Initial pH	Final Ph
2	4.1
4	4.67
6	6.34
8	7.6
10	8.9
12	11

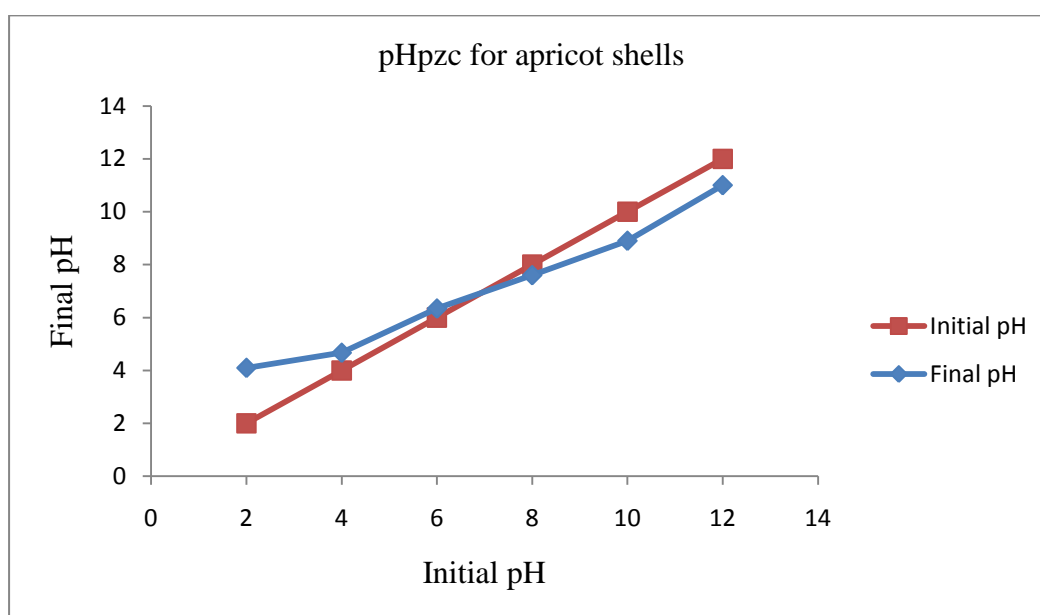


Fig. 5.2: pH_{pzc} for activated apricot shells

As it can be seen from the curve that initial pH line cuts the final pH line at a pH value which is around 6.8. So pH_{pzc} for the activated apricot shells is 6.8.

Table 5.10: pH_{pzc} for activated samples

Adsorbent	pH _{pzc}
Activated almond shells	6
Activated apricot shells	6.8

5.10 Fourier Transform Infrared Spectroscopy (FTIR):

In order to identify the organic or inorganic nature of chemicals FTIR is the most useful test. Using this method solid, liquid and gases can be analyzed. Collection of the data and its conversion from interference pattern to a spectrum is a recent development. Now a day's instruments involved in FTIR are computerized so the entire process becomes much faster and the sensitivity also increases as compared to the older dispersive instruments. In order to identify chemicals from spills, paints, polymers, coating, drugs and contaminants FTIR is most frequently used. It is also used to characterize the type of chemical bonds (functional groups).

It is a method in which an infrared spectrum of absorption or emission of a solid liquid or gas can be obtained. An FTIR spectrometer has a significant advantage over a dispersive spectrometer as it can collect high spectral resolution data simultaneously over a wide spectral range unlike a dispersive spectrometer which measures intensity over a narrow range of wavelength.

As the method requires the conversion of raw data into the actual detailed spectrum using Fourier transforms so the term Fourier Transform Infrared spectroscopy originates.

The important characteristics of the chemical bonds are the wavelength of light absorbed and is visualised in the annotated spectrum. In order to determine the chemical bonds in the molecules interpretation is required to be done of the infrared absorption spectrum. It shall also be noted that the FTIR spectrum of pure compounds are peculiar and unique. Due to this they are also termed as a molecular fingerprint. While doing the FTIR analysis of several compounds it has been found that organic compounds have a very rich and detailed spectrum but for inorganic compounds the spectrum is simple and is not very detailed.

The identification of the functional groups can be done by the comparison of the spectra of unknown compound with a library of known compounds. In order to identify those materials which are less common this method of infrared spectroscopy needs to be combined with other techniques like nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X ray diffraction and several other techniques.

In order to carry out the FTIR analysis IPRrestige-21, FTIR- 84005, SHIMADZU Corporation was used.

Steps for FTIR analysis:

- A 0.1gram sample of activated almond and apricot shells is taken.
- It is then mixed with 1gram of potassium bromide in a mortar.
- This mix is then placed in a cell connected to a hydraulic pump piston which gives a compression pressure of 15000pa/cm².
- This mix is then transformed in a solid disc and is then placed in an oven at 105 degree Celsius for 4 hours. This entire process is done to avoid any interference with any existing water vapour or carbon dioxide molecules.
- The above mix is then placed in a FTIR analyzer and a chromatogram is obtained corresponding to it. This chromatogram displays the wavelength of different functional groups in the sample which is then characterized by comparing these values with those in library.

An FTIR spectrum of activated almond and apricot shells is shown in appendix 1 and appendix 2. It has been seen that FTIR spectra of activated apricot shells is having a higher number of sharp bands in comparison to the activated almond shells. This spectrum requires its comparison with the values in library in order to identify the various functional groups in it.

Analysis of FTIR spectra of activated almond shells:

- A sharp crest at 666.51 cm⁻¹ can be associated with out of plane C-H bending mode.
- A sharp band at 1191.2 cm⁻¹ can be attributed to either C-O symmetric and asymmetric stretching vibrations.
- A sharp band at 1437 cm⁻¹ can be an indicator of presence of amides on the surface of activated almond shells.
- A sharp band at 1596 cm⁻¹ can be attributed to aromatic carbon carbon stretching vibrations.

Analysis of FTIR spectra of activated apricot shells:

- A sharp band at 2936.7 cm^{-1} can be associated with C-H interaction on the carbon surface.
- Band at 2858.9 cm^{-1} can also be associated to hydrogen bonded OH group of alcohol and phenol.
- Band at 1592.8 cm^{-1} can be attributed to carbon carbon stretching vibrations.
- A sharp adsorption band at 1314.2 cm^{-1} is associated with either C-O symmetric or asymmetric stretching vibrations.
- A sharp band at 1129.8 cm^{-1} can be associated to either Si-O or C-O stretching in alcohol, ether or hydroxyl group.
- A hazy region in $450\text{-}750\text{ cm}^{-1}$ is associated with in plane and out of plane aromatic ring deformations and vibrations.

6. Removal experiments and observations:

The main aim of the entire study is to analyze the suitability of the almond and apricot shells that have been activated using physical activation methods for the removal of hexavalent chromium.

In order to carry out the removal experiments, following chemicals and reagents were required.

- Potassium dichromate standard solution: In order to prepare a standard solution of potassium dichromate having a concentration of 50mg/l, 141.346 gram of dried potassium dichromate is taken in reagent water and diluted to 1 litre. This serves as a stock solution for hexavalent chromium and potassium dichromate solution of required strength can be prepared by suitably diluting the stock solution.
- Diphenyl Carbazide solution: 250 mg of 1-5 Diphenyl Carbazide (DPC) is dissolved in 50 ml of acetone to obtain the DPC solution.
- Sulphuric acid: 10 ml of reagent grade sulphuric acid is diluted to 100 ml.

The overall strategy that was adopted for removal of hexavalent chromium is as following:

- Optimization of pH: Hexavalent chromium solution is adjusted to different pH values. It is then added to a fixed dose of adsorbent and the suspension thus prepared is subjected to shaking in the mechanical shaker at a speed of 150 rpm for a fixed time of 30 minutes. After shaking, the sample was centrifuged for 15 minutes at 5000 rpm to obtain a clear residue, to which dilute sulphuric acid and Diphenyl Carbazide was added which leads to colour development. This was then analyzed in spectrophotometer to find out the residual concentration of hexavalent chromium. The pH corresponding to which least concentration of hexavalent chromium was found is termed as optimum pH and further studies are to be carried out at this pH value.

- Optimization of contact period: Hexavalent chromium solution that has been adjusted to optimum pH value as obtained above is then added to a fixed dose of activated almond and apricot shells. The suspension thus prepared is then subjected to shaking in a mechanical shaker at a speed of 150 rpm for varying contact times. After shaking, the sample was centrifuged for 15 minutes at 5000 rpm to obtain a clear residue, to which dilute sulphuric acid and Diphenyl Carbazide was added which leads to colour development. This was then analyzed in spectrophotometer to find out the residual concentration of hexavalent chromium. The contact period corresponding to which least concentration of hexavalent chromium was found is termed as optimum contact period and further studies are to be carried out for this value of contact period between activated adsorbents and the adsorbate .
- Optimization of the adsorbent dose: Hexavalent chromium solution that has been adjusted to optimum pH value is added to fixed dose of activated almond and apricot shells. The suspension thus prepared is then subjected to shaking in a mechanical shaker at a speed of 150 rpm at room temperature for the optimized contact period that has been found earlier. After shaking, the sample was centrifuged for 15 minutes at 5000 rpm to obtain a clear residue, to which dilute sulphuric acid and Diphenyl Carbazide was added which leads to colour development. This was then analyzed in spectrophotometer to find out the residual concentration of hexavalent chromium. The adsorbent dose corresponding to which least concentration of hexavalent chromium was found is termed as optimum adsorbent dose and further studies are to be carried out for this value of adsorbent dose.
- Optimization of temperature: Hexavalent chromium solution that has been adjusted to optimum values of pH, and dosages of activated almond and apricot shells is subjected to shaking in a mechanical shaker at varying temperature conditions for the optimum contact period that has been obtained earlier. After shaking, the sample was centrifuged for 15 minutes at 5000 rpm to obtain a clear residue, to which dilute sulphuric acid and Diphenyl Carbazide was added which leads to colour development. This was then analyzed in spectrophotometer to find out the residual concentration of hexavalent chromium. The temperature corresponding to which least concentration of hexavalent chromium was found is

termed as optimum temperature. As the adsorption process is dependent on temperature so further studies should be carried out for this value of temperature.

6.1 Optimization of pH

Following steps were adopted for the optimization of pH

- 10 ml of standard stock solution of 50 mg/l was taken in three conical flasks each and was diluted 10 times to obtain a hexavalent chromium solution having the concentration of 5 mg per litre.
- An initial dose of 0.5 gm of activated almond shells was then added to the three flasks having the chromium solution of above concentration.
- In a similar manner suspensions of activated apricot shells were also prepared.
- pH of the suspensions that have been prepared is measured.
- pH of the suspensions is then adjusted to the value of 5, 7 and 10 by the addition of an acid (dilute HCL) or base (NaOH).
- After the pH has been adjusted, conical flasks containing the suspensions of activated almond and apricot shells are then placed in a mechanical shaker and are subjected to shaking.
- Initial speed maintained is 150 rpm and contact duration is 30 minutes.
- After 30 minutes the flasks are taken out from the shaker and are then placed in a centrifuge.
- The suspensions are kept in the centrifuge for a period of 15 minutes and speed is maintained at 5000 rpm. However in order to obtain a clearer supernatant this entire process can be repeated once again.
- After centrifugation the clearer supernatant corresponding to different pH value is then transferred to another flask.
- This is followed by the addition of 0.5 ml each of Diphenyl Carbazide and sulphuric acid.
- This leads to development of pink colour in the supernatant which is left undisturbed for half an hour so that colour develops uniformly.
- This is to be analyzed for the residual concentration of copper using spectrophotometer.

- A separate blank solution of distilled water with addition of DPC and sulphuric acid is prepared. Corresponding to this blank solution the percentage transmittance should be 100.
- Now the supernatants in which colour has been developed are analyzed for the residual chromium concentration.
- The pH value corresponding to one having least residual concentration of chromium is noted and this pH value is reported as the optimum pH.

Table 6.1: pH optimization for activated almond shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (grams)	Temperature (degree Celsius)	Final chromium concentration (mg/l)
5	5	30	0.5	30	3.6913
5	7	30	0.5	30	4.4288
5	10	30	0.5	30	4.2088

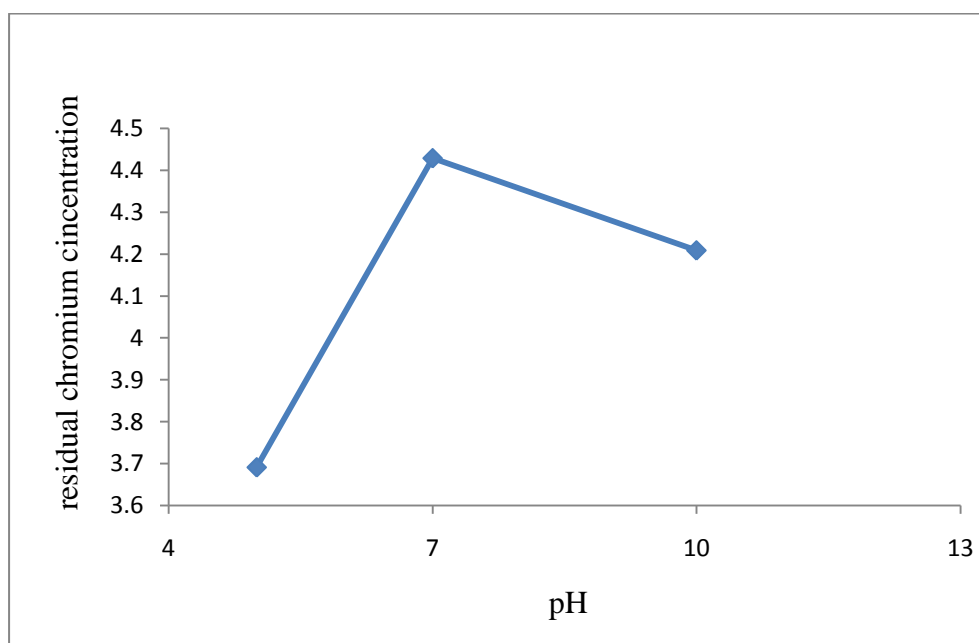


Fig. 6.1: pH optimization for activated almond shells

As it can be concluded from the graph that for pH 5, least residual concentration of chromium is obtained. So 5 is the optimum value of pH. Thus all the subsequent steps for

optimization of contact period, adsorbent dose and temperature shall be carried out at this value of pH.

Table 6.2: pH optimization for activated apricot shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gram)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	30	0.5	30	3.8499
5	7	30	0.5	30	4.5753
5	10	30	0.5	30	4.3488

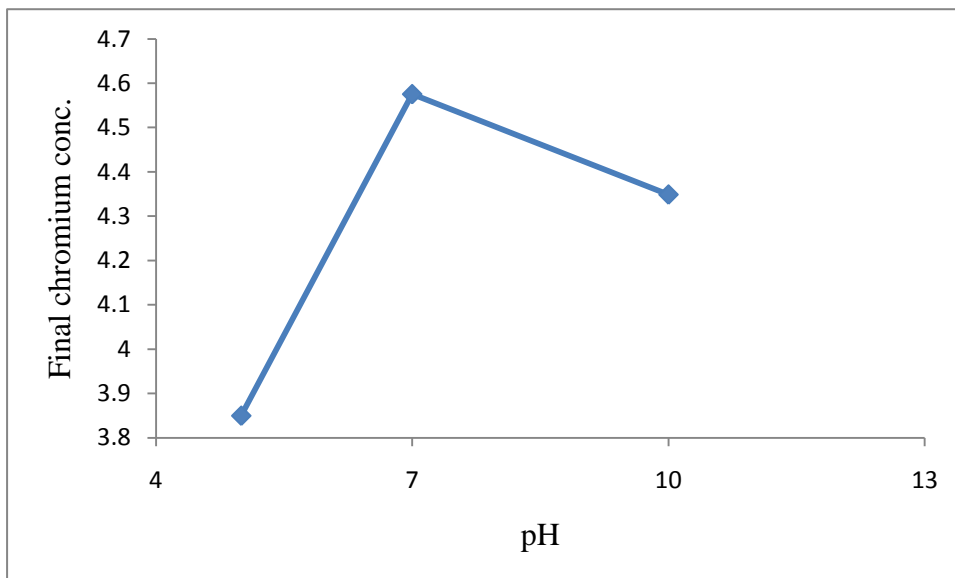


Fig. 6.2: pH optimization for activated apricot shells

As it can be concluded from the graph that for pH 5, least residual concentration of chromium is obtained. So 5 is the optimum value of pH. Thus all the subsequent steps for optimization of contact period, adsorbent dose and temperature shall be carried out at this value of pH.

For both, activated almond and apricot shells the optimum pH value is 5.

6.2 Optimization of contact period:

- 10 ml of standard stock solution of 50 mg/l was taken in four conical flasks each and was diluted 10 times to obtain a hexavalent chromium solution having the concentration of 5 mg per litre.
- An initial dose of 0.5 gm of activated almond shells was then added to the three flasks having the chromium solution of above concentration.
- In a similar manner suspensions of activated apricot shells were also prepared.
- pH of the suspensions that have been prepared is measured.
- pH of the suspensions is then adjusted to the optimum value of 5 by the addition of an acid (dilute HCL) or base (NaOH).
- The flasks are then placed in a mechanical shaker and initial speed of 150 rpm is maintained and contact period is varied. The contact period that is taken is 15 minutes, 30 minutes and 1 hour.
- After 15 minutes, 30 minutes and 1 hour the flasks are taken out from the shaker and are then placed in a centrifuge.
- The suspensions are kept in the centrifuge for a period of 15 minutes and speed is maintained at 5000 rpm. However in order to obtain a clearer supernatant this entire process can be repeated once again.
- After centrifugation the clearer supernatant corresponding to different contact period is then transferred to another flask.
- This is followed by the addition of 0.5 ml each of Diphenyl Carbazide and sulphuric acid.
- This leads to development of pink colour in the supernatant which is left undisturbed for half an hour so that colour develops uniformly.
- This is to be analyzed for the residual concentration of copper using spectrophotometer.
- A separate blank solution of distilled water with addition of DPC and sulphuric acid is prepared. Corresponding to this blank solution the percentage transmittance should be 100.
- Now the supernatants in which colour has been developed are analyzed for the residual chromium concentration.

- The contact period corresponding to one having least residual concentration of chromium is noted and this value is reported as the optimum contact period.

Table 6.3: contact period optimization for activated almond shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gram)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	15	0.5	30	3.8641
5	5	30	0.5	30	3.4832
5	5	45	0.5	30	3.7342
5	5	60	0.5	30	4.4057

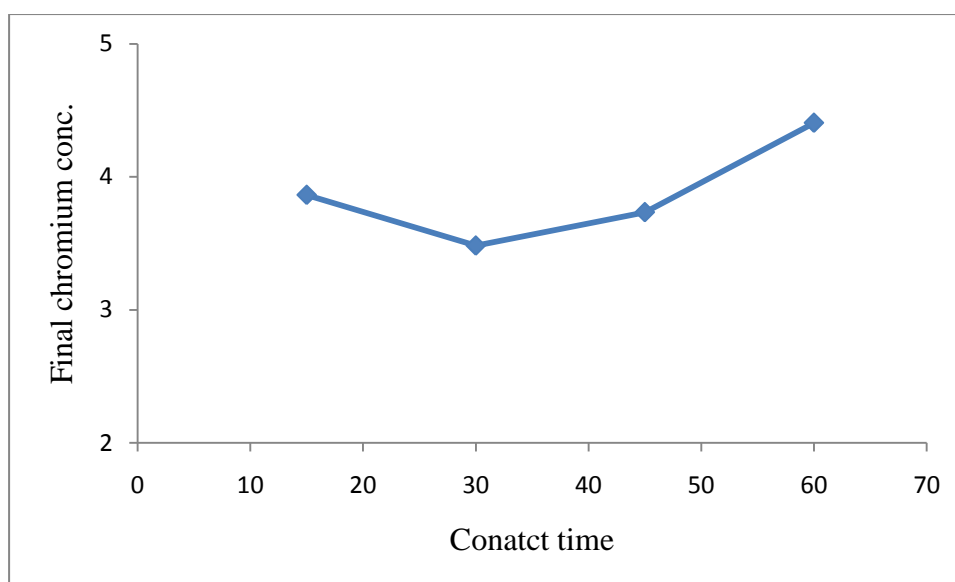
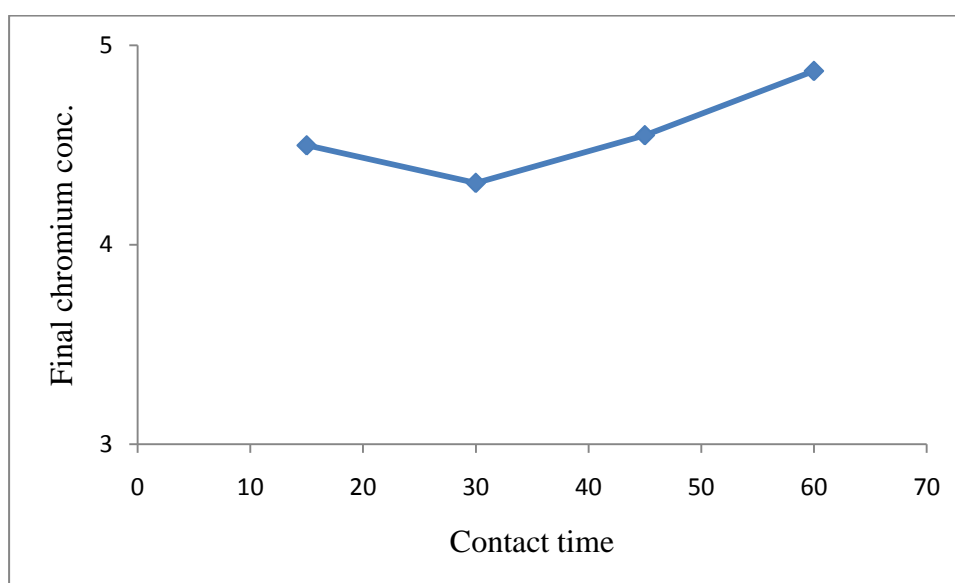


Fig. 6.3: contact period optimization for activated almond shells

From the above graph it can be concluded that least value of residual chromium concentration is obtained corresponding to a contact period of 30 minutes. Thus, the optimized value of contact period is 30 minutes. All the subsequent analysis of adsorbent dose optimization and determination of optimum value of temperature are to be done with a contact period of 30 minutes and at an optimum pH value of 5.

Table 6.4: Contact period optimization for activated apricot shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gram)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	15	0.5	30	4.4983
5	5	30	0.5	30	4.3102
5	5	45	0.5	30	4.5492
5	5	60	0.5	30	4.8713

**Fig. 6.4:** Contact period optimization for activated apricot shells

From the above graph it can be concluded that least value of residual chromium concentration is obtained corresponding to a contact period of 30 minutes. Thus, the optimized value of contact period is 30 minutes. All the subsequent analysis of adsorbent dose optimization and determination of optimum value of temperature are to be done with a contact period of 30 minutes and at an optimum pH value of 5.

It is concluded that optimum value of contact period for activated almond and apricot shells is 30 minutes.

6.3 Adsorbent dose optimization:

- 10 ml of standard stock solution of 50 mg/l was taken in four conical flasks each and was diluted 10 times to obtain a hexavalent chromium solution having the concentration of 5 mg per litre.
- An initial dose of 0.25 gram, 0.5 gram, 0.75 gram and 1 gram of activated almond shells was then added to the three flasks having the chromium solution of above concentration.
- In a similar manner suspensions of activated apricot shells were also prepared.
- pH of the suspensions that have been prepared is measured.
- pH of the suspensions is then adjusted to the optimum value of 5 by the addition of an acid (dilute HCL) or base (NaOH).
- The flasks are then placed in a mechanical shaker and initial speed of 150 rpm is maintained at the optimum contact period of 30 minutes.
- After 30 minutes the flasks are taken out from the shaker and are then placed in a centrifuge.
- The suspensions are kept in the centrifuge for a period of 15 minutes and speed is maintained at 5000 rpm. However in order to obtain a clearer supernatant this entire process can be repeated once again.
- After centrifugation the clearer supernatant corresponding to different adsorbent dose is then transferred to another flask.
- This is followed by the addition of 0.5 ml each of Diphenyl Carbazide and sulphuric acid.
- This leads to development of pink colour in the supernatant which is left undisturbed for half an hour so that colour develops uniformly.
- This is to be analyzed for the residual concentration of copper using spectrophotometer.
- A separate blank solution of distilled water with addition of DPC and sulphuric acid is prepared. Corresponding to this blank solution the percentage transmittance should be 100.
- Now the supernatants in which colour has been developed are analyzed for the residual chromium concentration.

- The adsorbent dose corresponding to one having least residual concentration of chromium is noted and this value is reported as the optimum adsorbent dose.

Table 6.5: Adsorbent dose optimization for activated almond shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gm)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	30	0.25	30	3.9374
5	5	30	0.50	30	3.7637
5	5	30	0.75	30	3.9854
5	5	30	1.00	30	4.0754

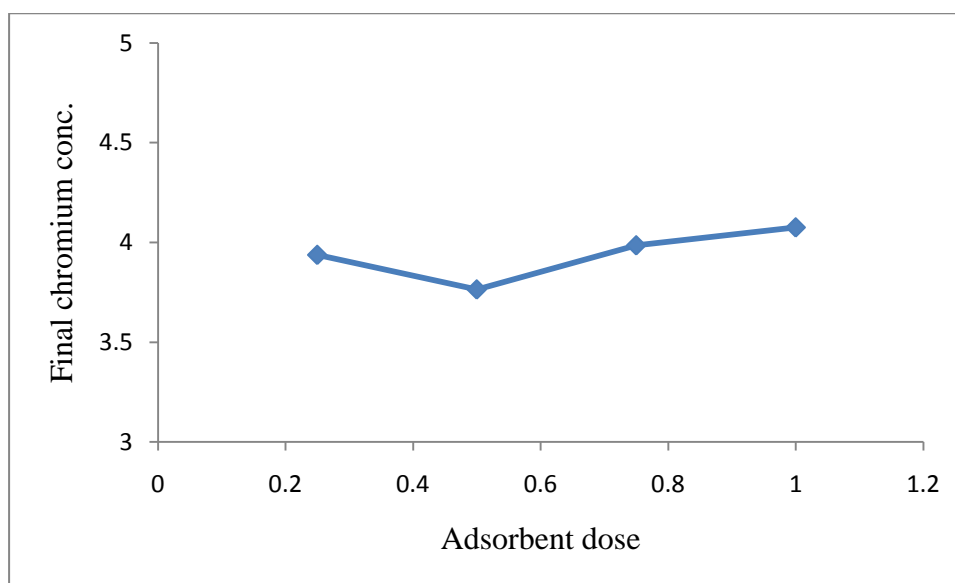
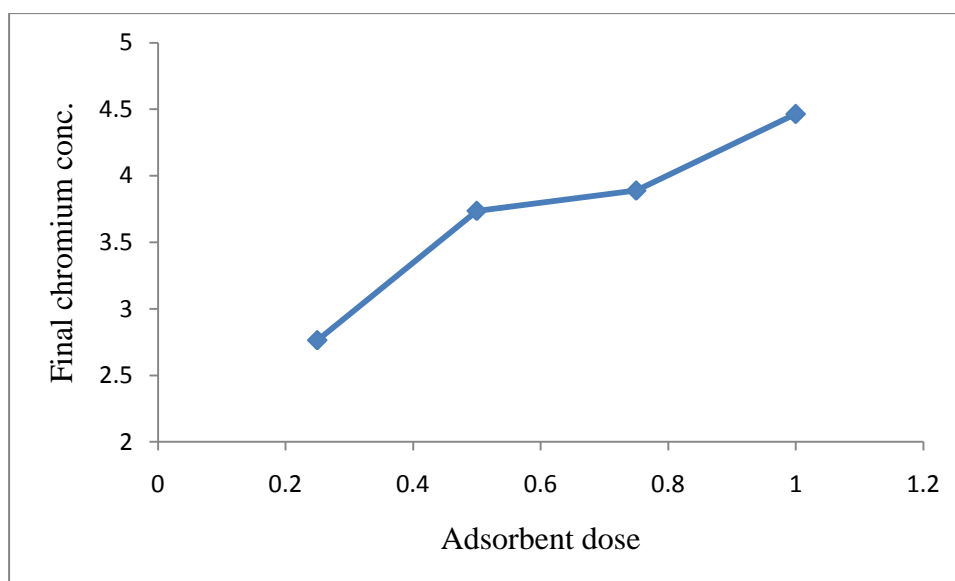


Fig. 6.5: Adsorbent dose optimization for activated almond shells

From the above graph it can be concluded that least value of residual chromium concentration is obtained corresponding to adsorbent dose of 0.5 gram. Thus, the optimized value of adsorbent dose is 0.5 gram. The subsequent analysis of temperature optimization is to be done at the dose of 0.5 gram of activated almond shells.

Table 6.6: Adsorbent dose optimization for activated apricot shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gm)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	30	0.25	30	2.7641
5	5	30	0.50	30	3.7637
5	5	30	0.75	30	3.8894
5	5	30	1.00	30	4.4654

**Fig. 6.6:** Adsorbent dose optimization for activated apricot shells

From the figure it can be seen that the least value of residual chromium concentration is obtained corresponding to a dose of 0.25 grams of activated almond shells. Thus, the optimized value of adsorbent dose is 0.25 gram. The subsequent analysis of temperature optimization is to be done at the dose of 0.25 gram of activated almond shells.

The optimum dose for activated almond shells is 0.5 grams and optimum dose for activated apricot shells is 0.25 grams.

6.4 Temperature optimization

- 10 ml of standard stock solution of 50 mg/l was taken in three conical flasks each and was diluted 10 times to obtain a hexavalent chromium solution having the concentration of 5 mg per litre.
- The optimum dose of 0.5 grams of activated almond shells and 0.25 grams of activated apricot shells was added to it to prepare the suspension.
- pH of the suspensions that have been prepared is measured.
- pH of the suspensions is then adjusted to the optimum value of 5 by the addition of an acid (dilute HCL) or base (NaOH).
- The flasks are then placed in a mechanical shaker and initial speed of 150 rpm is maintained at the optimum contact period of 30 minutes.
- The temperature is varied for this case. One of flask is kept at a temperature of 15 degree Celsius, the other two at a temperature of 30 degree Celsius and 45 degree Celsius.
- After 30 minutes the flasks are taken out from the shaker and are then placed in a centrifuge.
- The suspensions are kept in the centrifuge for a period of 15 minutes and speed is maintained at 5000 rpm. However in order to obtain a clearer supernatant this entire process can be repeated once again.
- After centrifugation the clearer supernatant corresponding to different adsorbent dose is then transferred to another flask.
- This is followed by the addition of 0.5 ml each of Diphenyl Carbazide and sulphuric acid.
- This leads to development of pink colour in the supernatant which is left undisturbed for half an hour so that colour develops uniformly.
- A separate blank solution of distilled water with addition of DPC and sulphuric acid is prepared. Corresponding to this blank solution the percentage transmittance should be 100.
- Now the supernatants in which colour has been developed are analyzed for the residual chromium concentration.
- The temperature corresponding to one having least residual concentration of chromium is noted and this value is reported as the optimum value of

temperature. So the entire removal operations should be carried out at this temperature for maximum efficiency.

Table 6.7: Temperature optimization for activated almond shells

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gm)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	30	0.50	15	3.6046
5	5	30	0.50	30	3.8086
5	5	30	0.50	45	2.8846

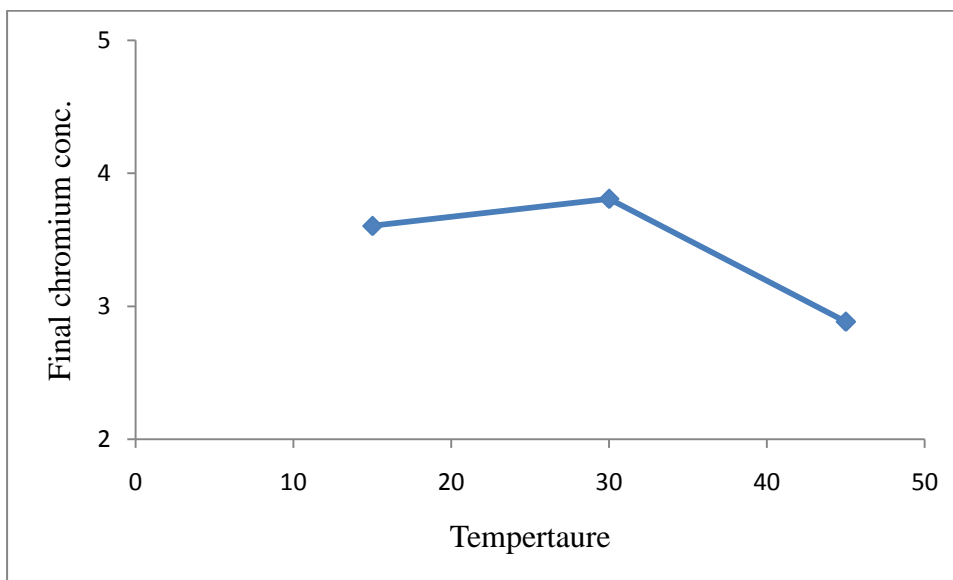
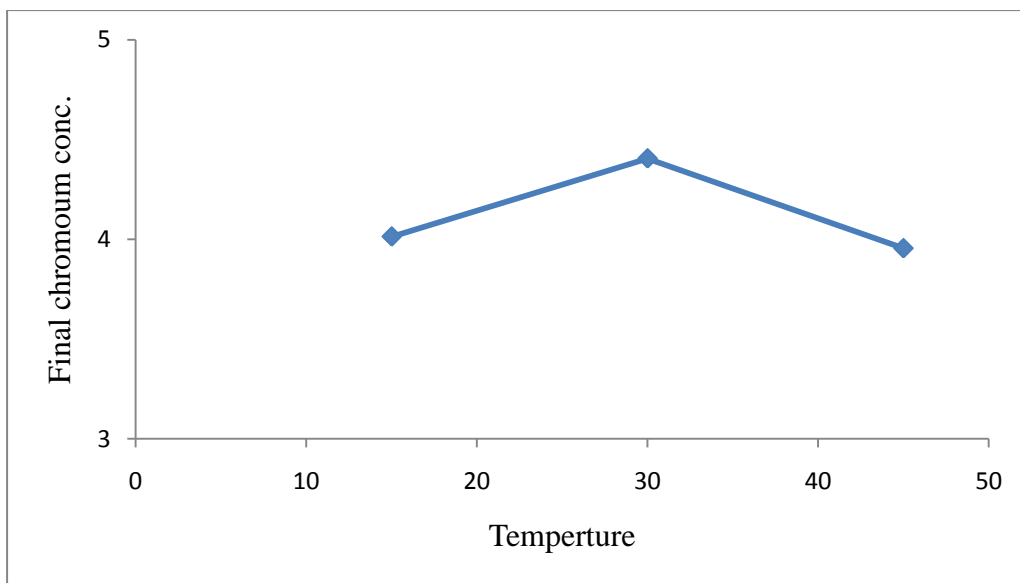


Fig. 6.7: Temperature optimization for activated almond shells

From the above figure it can be concluded that for activated almond shells, the least value of residual chromium concentration is obtained at a temperature of 45 degree Celsius. It is also seen that final chromium concentration at a temperature of 15 degree Celsius is lower than the concentration which is obtained at the room temperature condition. Thus the optimum value of temperature for the removal experiments is 45 degree Celsius.

Table 6.8: Temperature optimization for activated apricot shells:

Initial chromium concentration (mg/L)	pH	Contact period (minutes)	Adsorbent dose (gm)	Temperature (Degree Celsius)	Final chromium concentration (mg/L)
5	5	30	0.25	15	4.0134
5	5	30	0.25	30	4.4047
5	5	30	0.25	45	3.9546

**Fig.6.8:** Temperature optimization for activated apricot shells:

From the above figure it can be concluded that for activated apricot shells, the least value of residual chromium concentration is obtained at a temperature of 45 degree Celsius. It is also seen that final chromium concentration at a temperature of 15 degree Celsius is lower than the concentration which is obtained at the room temperature condition. Thus the optimum value of temperature for the removal experiments is 45 degree Celsius.

For activated almond and apricot shells both the optimum value of temperature is 45 degree Celsius.

6.5. Langmuir adsorption isotherm

Validity of Langmuir adsorption isotherm can be tested by plotting C_e/Q_e against C_e . A linear plot shows the applicability of isotherm.

- For activated almond shells

Table 6.9: Langmuir isotherm calculations for activated almond shells

S. no.	$Q_e = (C_0 - C_e) \times V/M$	C_e	C_e/Q_e
1.	0.422308	2.8846	6.8305
2.	0.279080	3.6046	12.916
3.	0.238280	3.8086	15.983

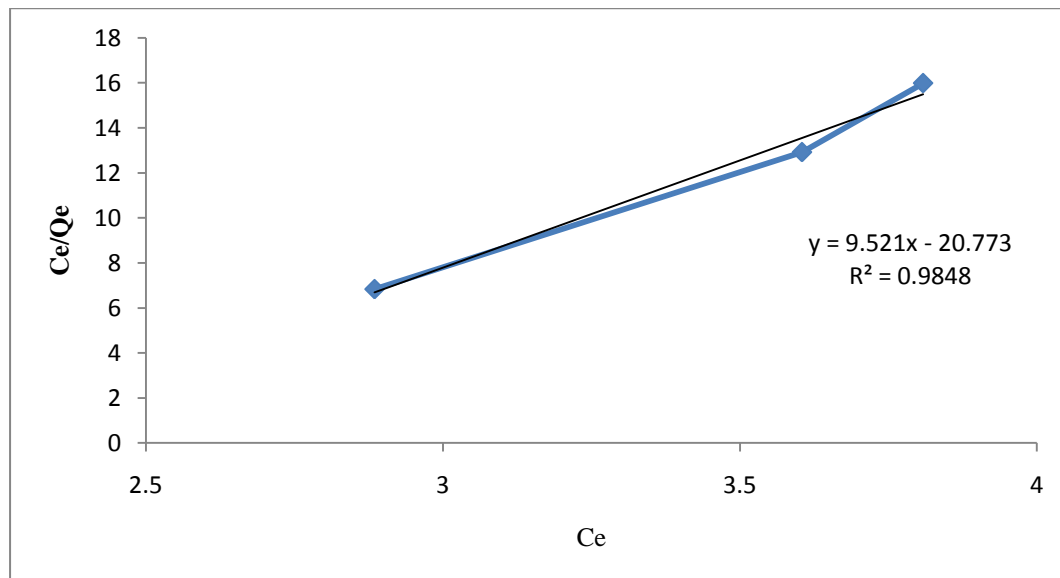


Fig.6.9: adsorption isotherm for almond shells

- For activated apricot shells

Table 6.10: Langmuir isotherm calculations for activated apricot shells

S. no.	$Q_e = (C_0 - C_e) \times V/M$	C_e	C_e/Q_e
1.	0.41816	3.9546	9.45710
2.	0.39464	4.0134	10.1697
3.	0.23812	4.4047	18.4978

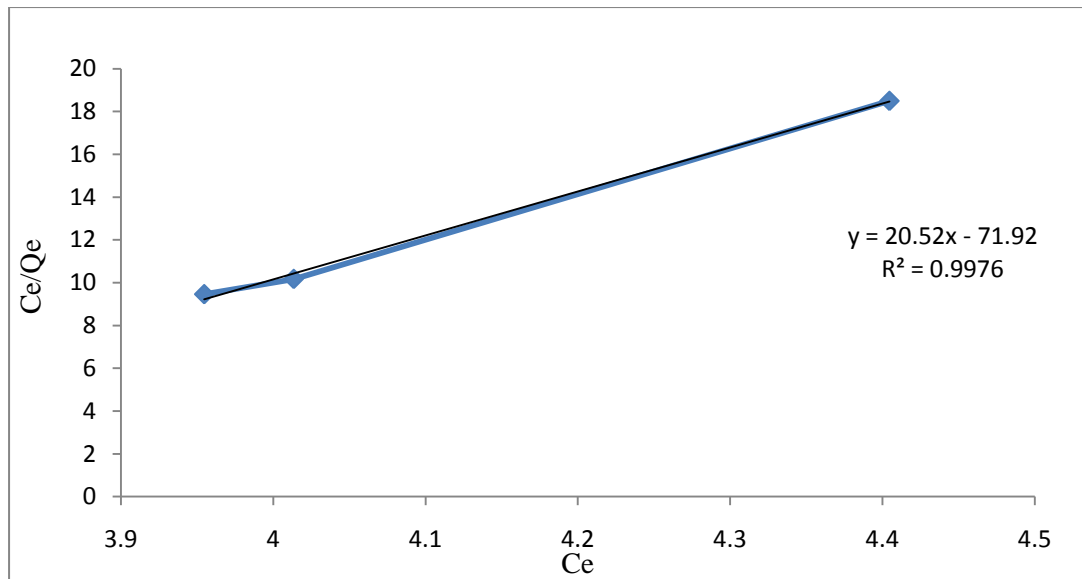


Fig.6.10: adsorption isotherm for apricot shells

As it can be seen from above figures, regression coefficient (R^2) value for adsorption experiments is 0.9848 using activated almond shells and 0.9976 using activated apricot shells. This high value of regression coefficient shows the applicability of Langmuir model.

7. Conclusion

In the present study, raw almond and apricot shells were activated using physical activation techniques. These activated shells were then characterized for their various physical and chemical properties. The suitability of these activated shells was then analyzed as an adsorbent and studies were conducted for removal of hexavalent chromium.

A Comparative study of the characteristics of activated almond and apricot shells is as shown in the following table.

Table 7.1: Properties of activated almond and apricot shells

Parameter	Activated almond shells	Activated apricot shells
pH	4.93	5.20
Electrical conductivity	195.90	173.20
Bulk density	0.49	0.41
Yield	39%	34%
Moisture content	9%	11%
Ash content	3.2%	3.7%
Iodine number	873.125	238.125
pHpzc	6	6.8

- As it can be seen from the table bulk density of activated almond shells is larger than that of apricot shells. Thus a large quantity of activated almond shells can be placed in a filter of given solid capacity.
- Yield of the activated almond shells is also higher than that of the apricot shells so for a given quantity of raw material more adsorbent can be generated from almond shells than apricot shells.

- The value of moisture content and ash content for the activated almond samples is smaller than that for the activated apricot samples signifying the better quality of the almond shells.
- Iodine number, which is an indicator of micro pore content and the degree of activation, has a higher value for the activated almond shells as compared to the apricot shells.
- Neither of the two activated samples exhibited the decolourizing tendency which is quite evident from Methylene blue number test.
- Also, the two prepared adsorbents differ in the nature of the functional groups on their surface as investigated in FTIR analysis.

The adsorption experiments were carried out in batch mode and the conditions were optimized for the activated almond and apricot shells.

- The optimum pH value to carry out the removal experiments for both activated almond and apricot shells was found to be 5.
- The optimum duration for contact time for both activated almond and apricot shells was found to be 30 minutes.
- The optimum dose for activated almond shells was found to be 0.5 gm for 100 ml chromium solution but the optimum dose for activated apricot shells was found to be 0.25 gm.
- The optimum temperature at which chromium removal was maximum for both activated almond and apricot shells was found to be 45 degree Celsius.
- The adsorption experiment is found to follow the Langmuir model for both activated almond and apricot shells.

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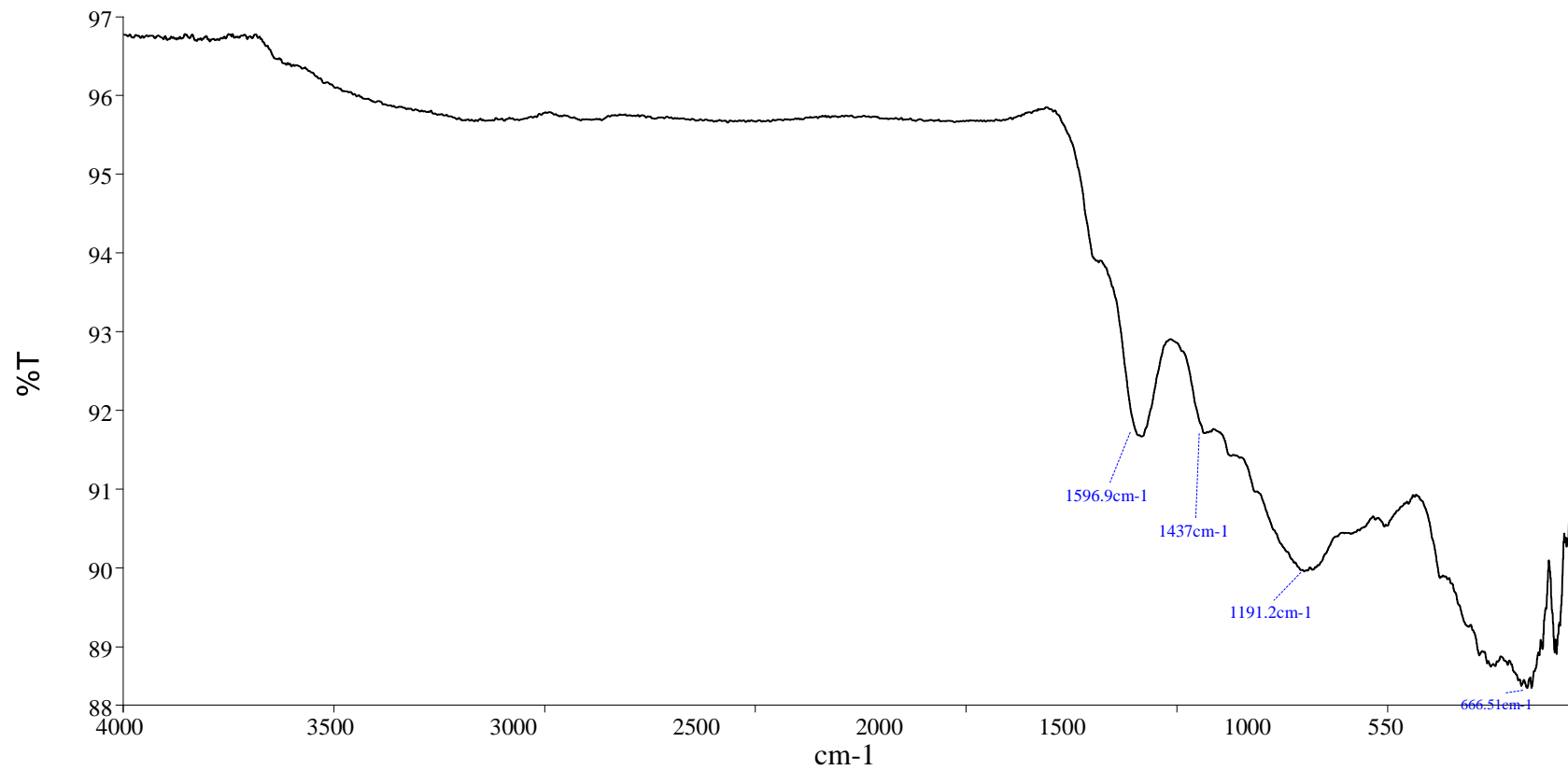
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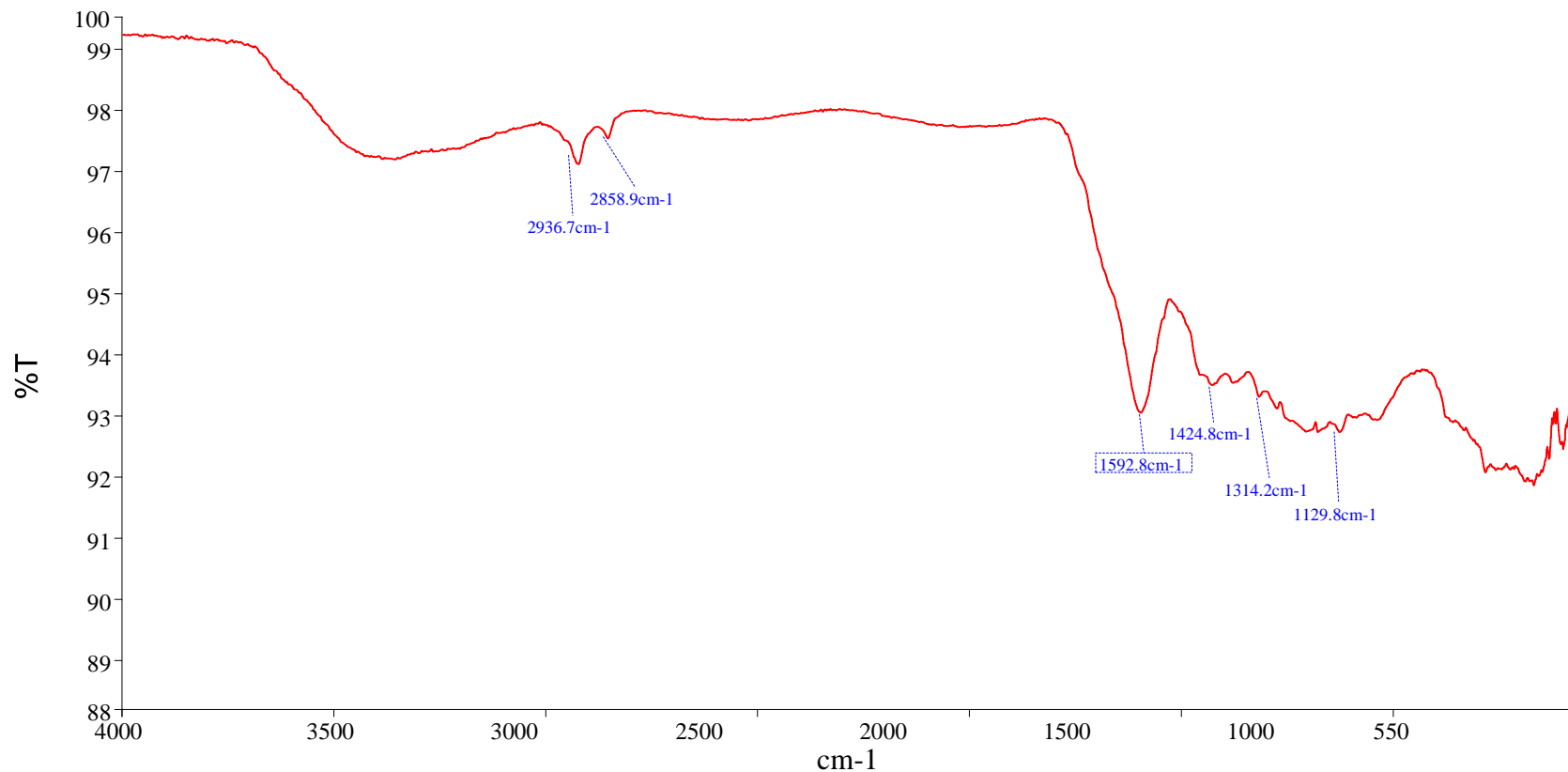
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