



Sudan University of Science and Technology

College of Graduate Studies



**Preparation of Activated Carbon from the Shell's Seeds of Ziziphus Spina
Christi and its Application in Removal of Cd²⁺ from Water**

تحضير الكربون المنشط من غلاف بذور النبق و استخدامه في إزالة ايونات الكاديوم من الماء

*A thesis submitted in partial fulfillment for the requirement of the degree of M.Sc.
in Chemistry*

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الآية

قال تعالى:

(اولم ير الذين كفروا ان السموات والارض كانتا رتقا ففتقناهما وجعلنا من الماء كل
شئ حي افلا يؤمنون)

صدق الله العظيم

(الانبياء... الآية 30)*

Dedication

I dedicated this work:

To my family members, specially my mother,

all people who supported and helped me

and my friends and research scholars

Acknowledgment

My special praise and thanks to Allah. I am deeply grateful to my supervisor: Dr. Mutasim Maknon Hassan for the support and guidance during the research. I would like to thank the technical staff in chemical and instrumental laboratory at Sudan University of Science and Technology and Khartoum University. I am also very grateful to Dr. Sahl Ibrahim who helped me a lot. I would like to acknowledge all my friends. Finally I am indebted to my family members for their support and encouragement throughout my life in all aspects, especially my mother who always keeps pushing me until I finished this research.

Abstract

In this research two types of activated carbon (AC) were prepared from Sudanese Nabag shells. The first one of AC was prepared by pregning the shells with sulphuric acid before carbonization. The second type of AC was prepared without chemical treatment.

The percentage yield of the products were calculated and found to be 32.31% for the AC treated with acid and 24.88 % for AC prepared without chemical treatment. The functional groups for the two carbons were determined by FT-IR technique and the results showed the presence of O-H, C-H and Si-O in the two types of AC.

The equilibrium time for the adsorption of cadmium ions at room temperature was determined and was found to be 20 minutes for the carbon prepared with acid and 10 minutes for the one prepared without chemical treatment. The adsorption efficiency and sorption capacity for these carbons was studied at different adsorbate concentrations. It was found that, the carbon prepared without acid showed a higher adsorptive capacity for removal of cadmium ions compared to the AC prepared with acid. They showed removal percentages of 50.2% and 14.77% at the same concentration and time respectively.

المستخلص

تم في هذه الدراسة تحضير نوعين من الكربون النشط بإستخدام غلاف بذور النبق السوداني. في النوع الاول تم معالجة غلاف بذور النبق بحمض الكبريتيك ثم حرقه. اما النوع الثاني فقد تم حرقه لتحضير الكربون دون معالجة كيميائية.

تم تحديد نسبة الناتج للنوعين ووجدت تساوي %32.31 و %24.88 علي التوالي.تم تحديد الزمر الوظيفية بتحليل الكربون بواسطة تقنية ال FT-IR وقد اظهرت النتائج وجود مجموعات O-H, C-H, Si-O وغيرها في النوعين. تم تحديد زمن اتزان الإدمصاص لانواع الكربون المحضرة وقد وجد ان الاتزان يحدث بعد 20 دقائق للكربون المحضر بالمعالجة بالحامض و 10 دقائق للمحضر دون معالجة كيميائية.

تم مقارنة كفاءة هذين النوعين من الكربون في إزالة ايون الكاديوم من الماء عند تراكيز مختلفة. وقد اظهرت النتائج ان الكربون المحضر دون معالجة كيميائية له كفاءة اكبر لإزالة ايون الكاديوم من الماء مقارنة بالكربون المحضر بالمعالجة الكيميائية. حيث وصلت نسبة الإزالة %50.2 باستخدام الكربون المحضر بدون معالجة كيميائية مقارنة بنسبة إزالة %14,77 باستخدام الكربون المعالج بالحامض عند نفس الزمن.

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Chapter One

Introduction

1.0 Introduction

Activated carbon (AC) is the general name applied to a group of porous carbons manufactured to exhibit a high degree of porosity and a large surface area (*Ferdi et al., 2002*). Activated carbon is a processed carbon material. Due to highly developed internal surface area and porosity, porous carbon materials or activated carbons have been used for thousands of years and have now become extremely versatile adsorbents. The adsorptive properties of carbon were well known long before the terms active and activated had been developed or adopted.

Activated carbon is a black solid substance resembling granular or powdered charcoal (*Abdulhalim et al., 2001*). The activated carbon can be produced from a large variety of raw materials with different pore sizes which can be achieved by using physical or chemical activation process or a combination of both of them. The physical activation method involves carbonization of the raw material and subsequent activation at high temperature in a carbon dioxide or steam atmosphere (*Carlos et al., 2001*).

Recently activated carbon becomes one of important materials due to its wide range of applications in the industries and environment. It is used to remove color, odor and taste from water (*Rang et al., 2007*). Generally, the raw materials used for AC production are these with high carbon and low inorganic content such as wood, peat and coal.

Many countries are producing AC in a commercial scale for exports. In Sudan there are many agricultural materials which can be used in AC production. Some of them can be used directly; in others the waste is used. Now there is a big demand for AC in Sudan due to the growing gold mining industries beside its application in water treatment. A wide range of materials are available in Sudan, from these the hard shells of Dome, Lalob, Nabag, Mango...etc. All these products are wastes of well known fruits in Sudan.

The presence of heavy metals in natural or industrial waste water is of major concern because of their toxicity and threat to human life and the environment. (*Arup & Gupta, 2002*). Many toxic metals have been discharged into the environment as industrial waste, causing serious soil and water pollution. Lead, copper, iron and

chromium are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (*Erdem et al., 2004*).

Anthropogenic sources of heavy metals include wastes from the electro plating and metal finishing industries, metallurgical industry, tannery operation, chemical manufacturing, mine drainage, battery manufacturing waste and leaches from landfills.

In recent years many researchers have studied the removal of different heavy metal ions including iron, chromium, nickel and copper from the water (*Baskaran et al., 2011*).

Many technologies are available for the removal of heavy metals from water and waste water such as ion exchange, adsorption, chemical precipitation, oxidation, reduction, reverse osmosis and electrolytic techniques (*Wesley, 1998*). Most of these processes can be less effective or difficult for practical use due to their high price and sludge disposal problem.

Therefore, to minimize this problem, lot of investigations has been carried out by the researchers to find out low cost easily available materials from agricultural waste along with industrial by products as adsorbents. Experimental adsorption properties of numerous biomass wastes have been reported, such as wheat bran, sawdust, sun flower stalk, onion skin, rice husk, banana pith and coconut shell to remove heavy metals from waste water.

Activated carbon adsorption is considered to be particularly competitive and effective process for the removal of heavy metals at trace quantities: however the used of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon.

Adsorption by activated carbon is an established treatment method for organic contaminants but has been rarely used in an actual treatment setting for organic adsorbates, despite the fact that the ability of activated carbons to removal heavy metals has been established by numerous researchers.

Chapter Two
Literature Review

2.0 Literature review

2.1 Activated carbon:-

Activated carbons (AC) are carbonaceous materials characterized by their extraordinarily large specific surface areas, well-developed porosity and tunable surface-containing functional groups. Hence they are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, potable water and wastewater (*Paul et al, 2015*). Although activated carbons have been extensively used as adsorbents, catalysts and catalyst supports in a variety of industrial and environmental applications (i.e. purification processes, recovery of chemical products, and removal of organic and metals), their adsorption capability and catalytic activity are shown to be largely controlled by their surface characteristics (*Nasrin et al., 2000*).

Activated carbon has been proven to be effective adsorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media. Their large sorption capacity is linked to their well developed internal structure, surface area and the present of a wide spectrum of surface functional groups.

Activated carbon prepared from solid wastes still is excellent adsorbents for many toxic materials present in the various types of waste water. The recent trend is the preparation of activated carbons from various kinds of wastes e.g. wood, coconut shells, nuts shells, cotton stalks ...etc.

2.2 Properties of activated carbon

2.2.1 The surface structure of Activated carbon:-

Activated carbon is a general term for a family of highly porous carbon across materials, none of which can be characterized by a structural formula or by chemical analysis. The volume of the pores in activated carbons is generally defined as being greater than 0.2ml/g and the internal surface area is generally larger than 400m²/g. The width of the pores varies from 3Å to several thousand angstroms (*Dougall, 1991*).

Activated carbons are commercially available in numerous form; powders, granular chips in various size range.

The adsorption capacities of activated carbon highly depend on the structure of AC.

2.2.2 Porous structure:-

Activated carbon has a random arrangement of micro crystallites with strong cross-linking between them and a well-developed porous structure. They have relatively low density (less than 2gm/cm³) and a low degree of graphitization. This porous structure formed during the carbonization process is developed further during the activation process.

Activated carbons are associated with pores starting from less than nanometer, Dublinin proposed a classification of the pores that has now been adopted by the international union of pure and applied chemistry (*IUPAC*). This classification is based on their width (w), the pores are divided into three groups:

The micro pores, the meso pores (transitional pores) and the macro pores (*Ramakrishna, 2012*).

Table (2.1)

Classification of pores according to their width (upac, 1972)

Type of pores	width
Micro pores	<2nm(20° a)
Meso pores	2-5nm(20-500° a)
Macro pores	>50nm(>500° a)

2.2.3 Crystalline structure:-

The crystalline structure of activated carbons differed from the graphite with respect to the interlayer spacing. The interlayer spacing ranges between 0.32 and 0.35 in active carbons, which is 0.335 in case graphite (*Ramakrishna, 2012*). The basic structural unit of ac is closely approximated by the structure of graphite. The graphite crystal is composed of layer of fused hexagons held by weak Van Der Waals forces shown in figure (2.1):-

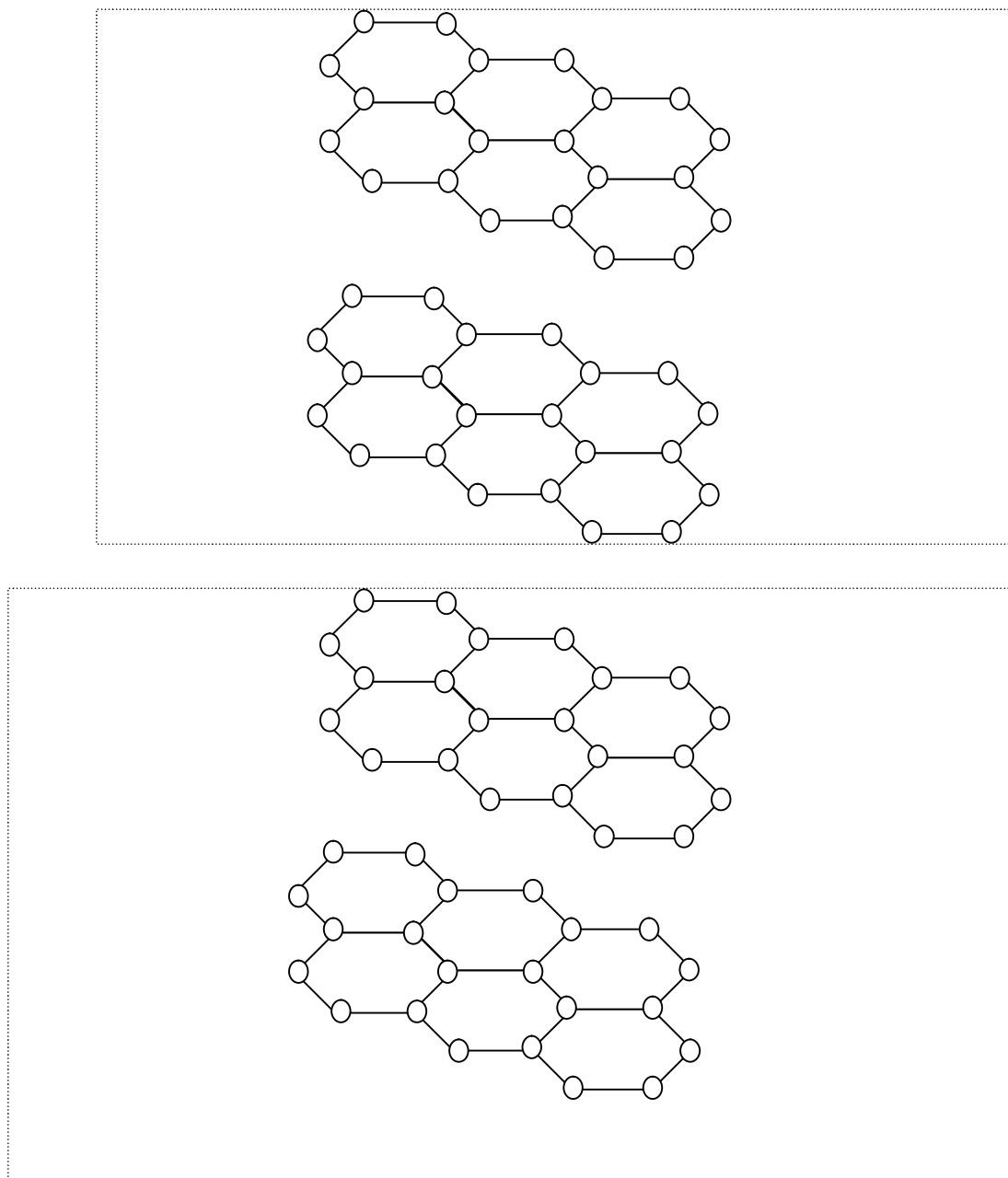


Figure (1) layered structure of graphite

Based on the graphitizing ability, activated carbon are classified into two types, graphitizing and non-graphitizing carbons. Graphitizing carbon had a large number of graphite layers oriented parallel to each other. The carbon obtained was delicate. Due to the weak cross linking between the neighbor micro crystallites and had a less-developed porous structure. The non-graphitizing carbon is hard due to strong cross-linking between crystallites and shows a well developed micro porous structure.

The formation of non-graphitizing structure with strong cross-links is promoted by the presence of associated oxygen or by an insufficiency of hydrogen.

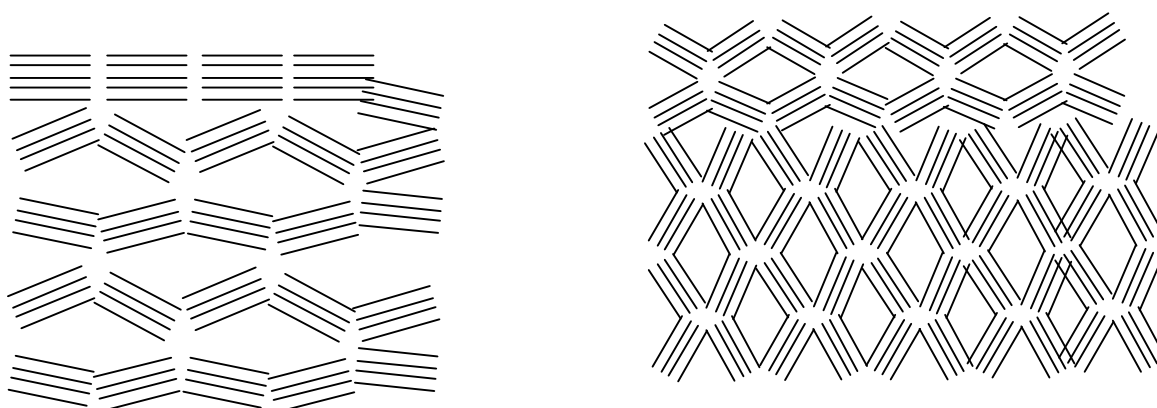


Figure (2) Schematic illustration structure of activated carbon:

(a) Graphitized carbon

(b) Non-graphitized carbon.

2.2.4 Chemical structure of the carbon surface:-

Besides the crystalline and porous structure, an activated carbon surface has a chemical structure as well. The adsorption capacity of active carbons is determined by their physical or porous structure but is strongly influenced by the chemical structure (Roop & Meenakshi, 2005).

Activated carbons are invariably associated with significant amounts of oxygen, hydrogen, halogens and other hetero atoms like sulfur, nitrogen, etc.

X-ray diffraction studies have shown that these hetero atoms or molecular species are bonded to the edge and corners of the aromatic sheets or to carbon atoms at defect positions and give rise to carbon-oxygen, carbon- hydrogen, carbon-nitrogen, carbon-

sulfur and carbon halogen surface compounds. These hetero atoms can also be incorporated within the carbon layers forming hetero cyclic ring systems.

2.3 Types of activated carbon:-

2.3.1 Powder activated carbon (PAC):-

With a small particle size PAC can be added to water at various locations in the water treatment process to provide time for adsorption to take place and then remove PAC by sedimentation or filtration (*John et al., 2005*).

PAC is made up of crushed or ground carbon particles such that 95-100% of it will pass through a designated sieve of 0.279mm according to the American Water Works Association (AWWA) standard. The average particle size of PAC being in the range of 15-25 μ m. PAC finds wide application in the treatment of both drinking water and wastewater. PAC is primarily used in the treatment of taste and odor compounds and the treatment of low concentrations of pesticides and other organic micro pollutants.

2.3.2 Granular activated carbon (GAC):-

GAC is usually in the form crushed granules of coal or shell ,GAC particles have sizes ranging from 0.2 to 5mm.gac is designated by mesh size such as 8/20, 20/40, or 40/60 for liquid phase application and 4/6, 4/8, or 4/10 for vapor phase application. Particle sizes in the range of 12/42 mesh are advantageous for liquid phase adsorption.

GAC filters are widely used in purification processes for drinking water and waste water as an advanced treatment step, particularly for the removal of toxic organic compounds (*Ferhan & Ozgur, 2012*).

2.4 Preparation of activated carbon:-

Generally activated carbon can be prepared from various raw materials including agricultural and forestry residues. Most of the precursors used for the preparation of activated carbon are rich in carbon. Production of activated carbon was achieved typically through two routes, physical activation and chemical activation.

2.4.1 Physical activation:-

By this process precursor is developed into activated carbon using gases. This is generally done by using one or a combination of the following processes: Carbonization: material having appreciable carbon content is pyrolyzed at temperature ranging between 600-900° C in the absence of oxygen (usually in inert atmosphere with gas like argon or nitrogen).

Activation/oxidation: In this process the raw material is exposed to oxidizing atmospheres (carbon mono oxide, oxygen or steam) at temperatures above 250° C usually in the temperatures range of 600-1200° C.

2.4.2 Chemical activation:-

Before carbonization, the row material can be impregnated with certain chemicals. The chemical needs to be typically an acid, strong base or salt (Phosphoric acid, sulfuric acid, potassium hydroxide, sodium hydroxide and zinc chloride....etc). After impregnation, the row material needs to be carbonized at lower temperatures 450-900°C. It is believed that the carbonization /activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

2.5 Factors affecting production of activated carbon:-

2.5.1 Raw material:

Most organic materials rich in carbon that do not fuse upon carbonization can be used as raw material for the manufacture of AC (*Nurul, 2007*). The selection of raw material for preparation of porous carbon, several factors are taken into consideration.

- i. High carbon content.
- ii. Low in inorganic content (i.e. low ash).
- iii. High density and sufficient volatile content.
- iv. The stability of supply in the countries.

- v. Potential extent of activation.
- vi. Inexpensive material.
- vii. Low degradation upon storage.

2.5.2 Temperature:-

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Generally, for commercial activated carbon usually conducted at temperature above 800⁰C in a mixture of steam and CO₂. As reported by several authors, activated temperature significantly affects the production yield of AC and also the surface area of activated carbon. The temperature used as low as 200⁰C and up to 1100⁰C.

2.5.3 Activation time:

Besides activation temperature, the activation time also affects the carbonization process and properties of AC. From the previous study the activation time normally used is from 1 hour to 3 hours for balm shell and coconuts. As the time increased, the percentage of yield increased gradually. This result is possibly due to the volatilization of organic materials from raw materials, which results in formation of activated carbon.

2.6 Application of activated carbon:-

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment air filters in gas masks and respirators, filters in compressed air and many other applications

Adsorption on activated carbon is an effective method for removing dissolved organic substances that cause taste and odor problems in drinking water (*Jerry, 2004*). It is also effective in removing the organic precursors that react with chlorine to form harmful THM compounds after disinfection.

When the carbon surfaces become covered with impurities the carbon can be cleaned or reactivated by heating to a high temperature in special furnace.

2.6.1 Liquid phase applications:-

Applications of activated carbons (AC) in liquid phase adsorptions are extensive, the number running into thousands. The following list indicates the wide ranging scenarios for AC:-

- (a) Drinking water availability, to improve taste, smell and color including removal of chlorinated compounds.
- (b) Improvements to ground water purity, contaminants coming from disused sites of heavy industries.
- (c) Treatments of both industrial and municipal waste water.
- (d) Mining operations require feed water treatment, metallic ion adsorption (gold and other metals) of excess fusion reagents.
- (e) Pharmaceutical processes, including purification of process water, use with fermentation broths and purification of many products.
- (f) The food, beverage and oil industries for removal of small, color and unacceptable tastes.
- (g) The dry-cleaning industries require purification of solvents.
- (h) The electro plating industries require purification of waste water containing Pb, Cr ...etc.
- (i) House hold water purification, cleaning of aquaria and use in oven-extract hoods.
- (j) The sugar and sweetener industries need de colorization agents for the production of white sugar ...etc.

2.6.2 Gas- phase application:-

It is impossible, in a single text, to describe adequately the large number of gas – phase application allocated to AC. The following list indicates the wide ranging scenarios for AC:-

- (a) Personal protection.
- (b) Cigarette filters.
- (c) Industrial gas masks.
- (d) Effluent gas purification.
- (e) Petroleum refineries.
- (f) Sewage and geothermal plants.
- (g) Organic and inorganic process catalysis, both as support material and as a catalyst.
- (h) Adsorption of radio nuclides.
- (i) Natural gas storage and purification.
- (j) Odor control generally.

Both GAC and PAC are used in liquid-phase application. Almost 60 wt % of the activated carbon used in USA for liquid –phase application is in powdered form. Liquid–phase application require AC with a large pore size than gas-phase ones, because of the need for rapid diffusion of the liquid to the interior of the carbon particles and because of the large size of many dissolved molecules to be retained.

2.7 Water pollution:

The term pollution is derived from the Latin word pollutes (pol means before and lutes means wash). The term water pollution is used to indicate an act of contaminating or making foul natural water bodies such as rivers, streams, wells...etc. (*Rang et al., 2007*). The pollution causes undesirable changes and it affects the land, water and air, or the environment as a whole. For healthy living the environment must be clean, scenic, refreshing and ecologically well-balanced.

Pollution means the addition of any foreign material (inorganic, biological or radiological) or any physical change in the natural water which may harmfully affect the living life (human, agricultural or biological) directly or indirectly.

In 1592 Couls and Forbes defined pollution as the addition of something to water which changes its natural qualities. In 1966 National Research Council Committee on pollution gave a report in which pollution is defined as an undesirable change in the physical, chemical or biological characteristics of our air, land and water that may or

will harmfully affect human life or that of other desirable species, our industrial processes, living conditions and cultural assets or that may or will wastes or deteriorates our raw material resources (*Kudesia, 2007*).

2.7.1 Sources of water pollution:-

The main water pollution sources are as under:

(a) Industrial waste.

(b) Domestic sewage.

Industrial effluent is the industrial waste coming from the industrial areas with big industries. It may contain grease, oil, chemicals, highly odorous substances, explosives... etc. When the waste of these industries is allowed to dispose off in river or any water source, they cause water pollution. Domestic sewage is also contains oils, human excreta, decomposed kitchen waste, soap, water, pathogenic bacteria from the sick people sewage, hospital sewage ...etc. If the domestic sewage is disposed off in the water sources, it will pollute them (*Birdie & Birdie, 2006*).

2.7.2 Classification of pollution:-

Water pollution can be classified as follows:-

(a) Physical pollution of water.

(b) Chemical pollution of water.

(c) Bacteriological pollution of water.

(a) Physical pollution:

The following factors are responsible for the physical pollution of water:

- (i) Color: The water may have color from natural or artificial sources. The colors discharge from tanneries, textile dyeing or such industries may cause color pollution.
- (ii) Temperature: Hot or warm water from thermal power station and various industries when discharge in rivers and other bodies of water may causes

increase in the water temperature. At high temperature the growth of the biological life is increased.

- (iii) Taste and odor: The water containing the taste and odor are objectionable and not liked by the public. This pollution do not have significant effect on the public health but it may kill the fish life.
- (iv) Turbidity: Finely divided suspended matter, colloidal matter, oxidized salts of iron and manganese, sewage and some industrial wastes cause turbidity in the water.

(b) Chemical pollution:

The organic or inorganic chemicals present in water may cause chemical pollution. This type of pollution may be due to the following:

- (i) Alkalis: The alkalis waste of industries when discharged in the body of water cause a chemical pollution. This pollution also has the same effect as of acids.
- (ii) Acids: The waste of some industries such as explosive factories, buttery industries... etc. contain acids, which when discharged in the body of water cause acidic pollution. This pollution causes corrosion of metal, concrete structures and affects the aquatic life.
- (iii) Toxic inorganic compound: Some waste of industries such as gas liquors, alkali products, ore ovens ...etc. are toxic to fish and other aquatic life. These industries wastes make the water toxic for any use.
- (v) Suspended organic substances: The particles of clay, silt, sand and others may cause pollution in the water.

2.8 Heavy metals:-

A heavy metal is any element in the d-block of the periodic table, or transition metals. Heavy metals are also known as toxic metals. These elements cause the environmental pollution from a number of sources, including industrial effluents, electro plating and tannery wastes.

Heavy metals don't normally undergo biological decay and are thus considered a challenge remediation, although few heavy metals such as, zinc and copper are required by human but excessive levels are hazardous. In the other hand, heavy metals such as, lead, and cadmium are toxic metals that have no known vital or beneficial effect on human beings, but their accumulation with time in the bodies of humans can cause several diseases.

2.8.1 Definition of heavy metals:-

Heavy metals are elements of high density, and they are toxic even at low concentration such as cadmium, lead, copper, mercury and chromium (*Mohamed, 2009*). Over the past two decades the term "heavy metals" has been widely used (*John, 2002*). It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity. At the same time, legal regulations often specify a list of heavy metals to which they apply. Such a list differs from one set of regulations to another and the term is sometimes used without even specifying which heavy metals are covered. However, there is no authoritative definition to be found in the relevant literature.

2.8.2 Heavy metals contamination:-

Heavy metals such as arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver are individual metals and metal compounds that can impact human health (*Sabine & Wendy, 2009*). All these are naturally occurring substances which are often present in the environment at low levels. Some of them contained in waste effluents of industrial processes. They can be dangerous if their concentrations are high in the environment.

Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing). Working in or living near an industrial site which utilizes these metals and their compound increases one risk of exposure, as does living near a site where these metals have been improperly disposed. Subsistence life styles can also impose higher risks of exposure and health impacts because of hunting and gathering activities.

Recently effort have been made to used cheap and available agricultural wastes such as orange peel, rice husk, peanut husk and sawdust as adsorbents to remove heavy metals from waste water (*Bernard et al., 2013*).

2.8.3 Effects of heavy metals on humans and the environment:-

The main threats to human health from heavy metals are associated with exposure to some heavy metals. From these; lead, cadmium, mercury, arsenic and chromium. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metals have been used by humans for thousands of years. Although several adverse health effects of heavy metals have been known in case of long time exposure to heavy metals contamination in some areas. For example, mercury is still used in gold mining in many parts of Latin America and Sudan also arsenic is still common in wood preservatives.

2.8.3.1 Cadmium:-

Cadmium is highly toxic non-essential metal which accumulates in the kidneys of mammals and can cause kidney dysfunction (*Mohammed Ali & Manar, 2013*).

Cadmium occurs naturally in ores together with zinc, lead and copper. Cadmium compounds are used as stabilizers in PVC products, color pigments, several alloys and now most commonly in re-chargeable nickel-cadmium batteries. Metallic cadmium has mostly been used as an anti-corrosion agent (cadmiation) (*Lars, 2003*).

The major exposure of cadmium for the non-smoking general population is via food; the contribution from other pathways to total uptake is small. Tobacco is an important source of cadmium uptake in smokers, as tobacco plants like other plants accumulate cadmium from the soil. Both human and animal studies indicate that skeletal damage (osteoporosis) may be a critical effect of cadmium exposure. Other effects of cadmium exposure are disturbances in calcium metabolism hypercalciuria and formation of renal stones.

The International Agency for Research on Cancer (IARC) classifies cadmium in class (1), the agent (mixture) is carcinogenic to humans. Occupational exposures are linked

to lung cancer and prostate cancer. According to a recent review, the epidemiological data linking cadmium and lung cancer are much stronger than for prostatic cancer, whereas are links between cadmium and cancer in liver, kidney and stomach are considered equivocal.

Cadmium is readily accumulated by many organisms, particularly by microorganisms and mollusks where the bio-concentrate cadmium is markedly. Cadmium is toxic to a wide range of microorganisms as demonstrated by laboratory experiments. The main effect is on growth and replication. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd^{2+} . Cadmium affects the growth of plants in experimental studies although no field effects have been reported. Stomata opening transpiration and photosynthesis have been reported to be affected by cadmium in nutrients solutions, but metal is taken up into plants more readily from nutrient solutions than from soil. Cadmium even at high dosage does not lethally affect birds, although kidney damage occurs. Cadmium has been reported in field studies to be responsible for changes in species composition in populations of microorganisms and some aquatic invertebrates. Leaf litter decomposition is greatly reduced by heavy metal pollution and cadmium has been identified as the most potent causative agent for this effect.

2.8.3.2 Chromium:-

Chromium occurs in a number of oxidation states, but trivalent chromium Cr^{3+} and hexavalent chromium Cr^{6+} are of the main biological relevance. There is a great difference between Cr^{3+} and Cr^{6+} with respect to toxicological and environmental properties. They must always be considered separately.

Chromium is similar to lead and is found bound to some particles. Chromium in general is not a bio accumulated metal and there is no increase in concentration of the metal in food chains. Contrary to the three other mentioned heavy metals, Cr^{3+} is an essential nutrient for man in amounts of 50-200 mg/day. Chromium is necessary for the metabolism of insulin. It is also essential for animals, but it is not know whether it is an essential nutrient for plants, although all plants contain the element.

Humans:

The kinetic of chromium depends on its oxidation state and the chemical and physical form within the oxidation state. Most of the daily chromium intake ingested with food is in the trivalent form. About 0.5 - 3% of the total intake of trivalent chromium is absorbed in the body. The gastrointestinal absorption of Cr^{6+} is 3 - 5 times greater than that of trivalent form; however some of it is reduced by gastric juice.

Skin exposure of the general public to chromium can occur from contact with products containing chromium such as leather or preserved wood or chromium containing soil. In general Cr^{3+} is considerably less toxic than Cr^{6+} . Cr^{6+} has been demonstrated to have number of adverse effects ranging from causing irritation to cancer.

Effects in humans occupationally exposed to high levels of chromium or its compound, primarily Cr (iv) by inhalation, may include irritating respiratory effects, possible circulatory effects, effects on stomach and blood, liver and kidney effects and increased risk of death from lung cancer.

Environment:-

Hexavalent chromium is in general more toxic to organisms in the environment than the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities, in air and pure water, but it is reduced to the trivalent state when it comes into contact with organic in biota, soil and water.

Hexavalent chromium is toxic to micro organisms; a property utilized in chromium - based bio acids .in general, toxicity for most microorganisms occurs in the range of 0.05-5mg chromium is less toxic than hexavalent.

2.8.3.3 Arsenic:-

Arsenic has been known as a highly toxic element for centuries and As (III) compound are more toxic than As (V). In spite of its toxicity, significant amounts of As compounds are still used in agriculture and industry. Recently, the effluent standard for As has been set to 0.1mg/l (0.001µ).

Arsenic compounds are present in waste water from metallurgical industry, glass ware and ceramic production, tannery operation, dyestuff manufacture, pesticide manufacture, organic and inorganic chemicals manufacture, petroleum refining and the rare-earth industry.

Toxicity:-

The toxicity of an arsenic containing compound depends on its valance state (zero-valent, trivalent or pentavalent), it's form (organic or inorganic), and factors that modify its absorption and elimination. Inorganic arsenic is generally more toxic than arsenic, and trivalent arsenic is more toxic than pentavalent and zero-valent arsenic.

Once absorbed into the body, arsenic undergoes some accumulation in soft tissue organs such as the liver, spleen, kidneys and lungs but the major long-term storage site for arsenic is keratin-rich tissues, such as skin, hair and nails.

2.9 Heavy metals removal technologies:-

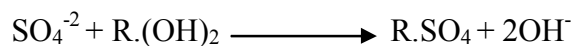
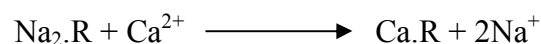
There are a number of technologies available for removal of heavy metals from water such as precipitation, ion exchange, reverse osmosis and adsorption. Chemical precipitation is most commonly employed for most of the metals. Common precipitants include hydroxide, sulfide and carbonate (*Wesley, 2000*). There is a whole range of treatment processes that can be used to treat water and remove heavy metals from water

2.9.1 Ion exchange:-

Ion exchange describes the physical-chemical process by which ions are transferred from a liquid phase to a solid phase and vice versa. Ions held by electrostatic forces to charged functional groups on the surfaces of a solid are exchanged for ions of like charge in a solution in which the solid is being contacted. Ion exchange resins consist of an organic or inorganic net work structure with attached functional groups.

Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Cationic exchange resins have acidic functional group, such as sulfonic, where as anionic exchange resins contain basic functional group, such as amine.

The reactions that occur depend upon chemical equilibrium situations in which one ion will selectively replace another on the ionized exchange site



2.9.1.1 Principal ion exchange materials:-

Ion exchange substances may have very varied origins. Reference here will be confined to a few of the principal types.

- 1- Certain natural sands (Glauconites and Aluminum silicates) the exchange capacity of which can be improved by appropriate treatment.
- 2- The synthetic aluminum silicates which generally have better exchange capacity than the natural substances.
- 3- Sulphonated carbons, prepared from bituminous, coal, peat and from all woody organic materials by treatment with hot fuming sulphuric acid.
- 4- Synthetic resins: there is a large number of synthetic resins suitable for ion exchange purpose, each of them having well-defined characteristics and special uses:
 - (a) The group of sulphonated phenol-formaldehyde resins.
 - (b) The group of carboxyl resins with very special characteristics.
 - (c) The polystyrene group of resins.
 - (d) Amine resins.

2.9.1.2 Ion exchange capacity:-

The exchange capacity of an ion exchange material in the weight of the ions (cations or anions as the case may be) which a unit volume of the material will exchange.

The ion exchange capacity is dependent on:-

- (a) The nature of the ion exchange material.
- (b) The rate of flow of water through the ion exchange material.
- (c) The mineral salt content of the liquid to be treated.
- (d) The method of regeneration reagent.
- (e) The quantity of regeneration reagent.

(f) The degree of purification desired.

2.9.2 Membrane technology:-

Membrane processes may involve physical separation phenomena (e.g. ultra filtration) or physical-chemical phenomena (e.g. reverse osmosis, electro dialysis). The latter are of most direct interest with respect to control of inorganic cationic toxicants. Reverse Osmosis (RO) is most widely applied for pollution control and product recovery.

RO has been proven to be the most economical technology not only for the desalination of water containing salts, but also for purifying water contaminated with heavy metals, pesticides and other contaminants.

2.9.2.1 How Reverse Osmosis Works:-

The phenomenon of osmosis (Fig 3) occurs when pure water flows from a dilute saline solution through a membrane into a higher concentrated saline solution.

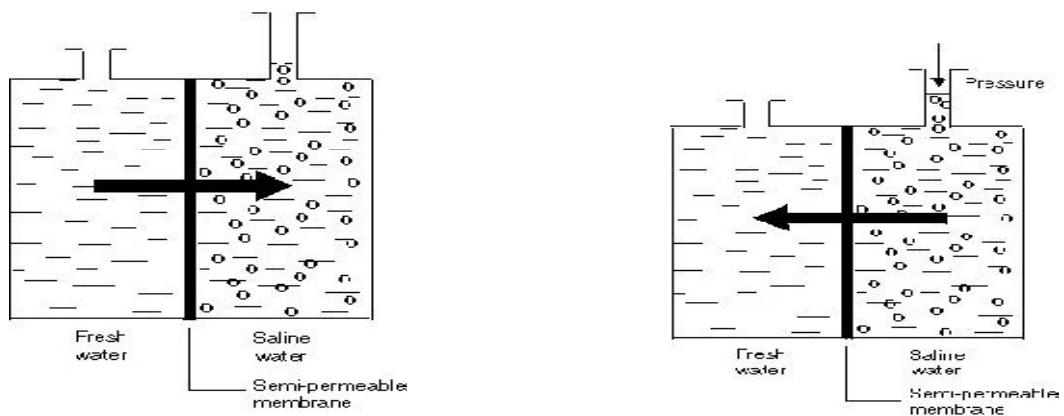


Fig (3): The theory of osmosis and reverse osmosis.

Reverse Osmosis (RO) is a membrane-based demineralization technique used to separate dissolved solids, such as ions, from solution. Membranes in general act as perm-selective barriers, that allow some species (such as water) to selectively permeate through them while selectively retaining other dissolved species (such as ions). Figure 1.1 shows how RO perm-selectivity compares to many other membrane-based and conventional filtration techniques. As shown in the figure, RO offers the finest filtration currently available, rejecting most dissolved solids as well as suspended solids. (Note that although RO membranes will remove suspended solids, these solids, if present in RO feed water, will collect on the membrane surface and foul the membrane (*Jane, 2010*)).

Reverse osmosis can be used to either purify water or to concentrate and recover dissolved solids in the feed water (known as "dewatering"). The most common application of RO is to replace ion exchange, including sodium softening, to purify water for use as boiler makeup to low- to medium-pressure boilers, as the product quality from an RO can directly meet the boiler make-up requirements for these pressures. For higher-pressure boilers and steam generators, RO is used in conjunction with ion exchange, usually as a pretreatment to a two-bed or mixed-bed ion exchange system. The use of RO prior to ion exchange can significantly reduce the frequency of resin regenerations, and hence, drastically reduce the amount of acid, caustic, and regeneration waste that must be handled and stored. In some cases, a secondary RO unit can be used in place of ion exchange to further purify product water from an RO unit. RO is also used to separate heavy metal ions from water and was found to be very effective even if the concentration is low.

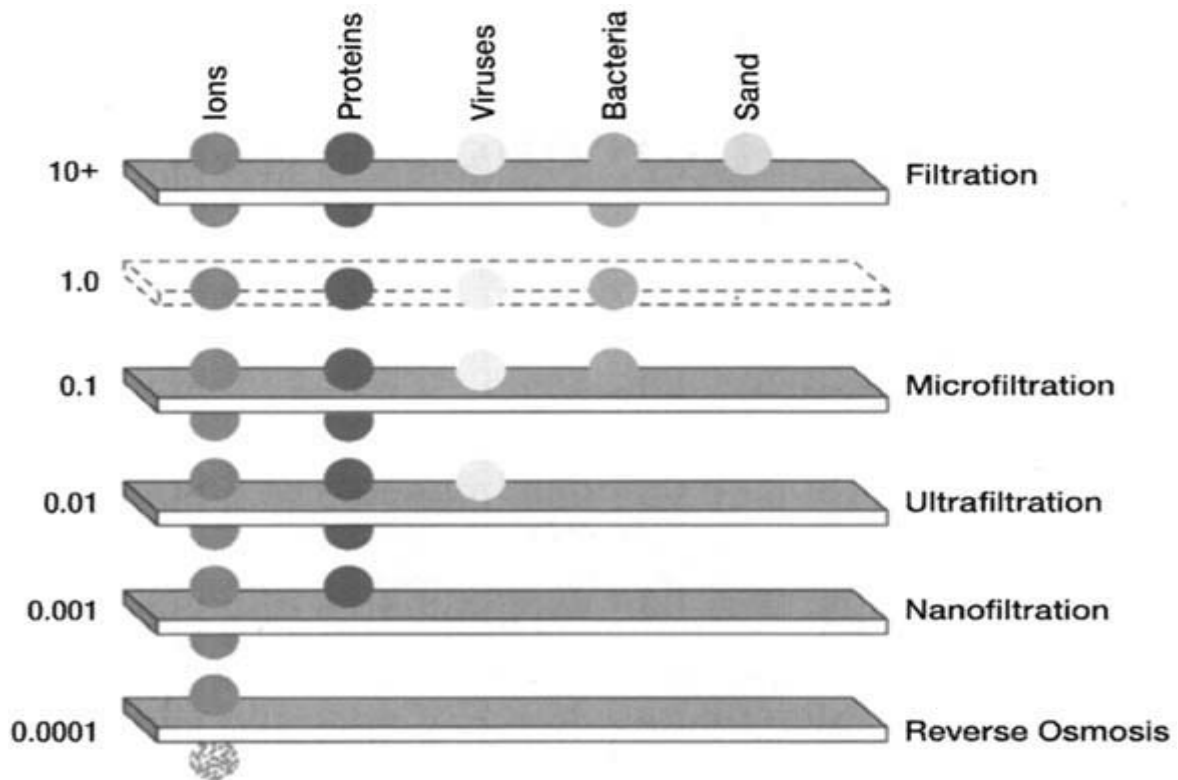


Figure (4): Filtration Spectrum comparing the rejection capabilities of reverse osmosis with other membrane technologies and with the separation afforded by conventional filtration.

2.9.3 Adsorption:-

Adsorption is a surface phenomenon that is defined as the increase in concentration of a particular component at the surface or interface between two phases (*Samuel & Osman, 1987*). The principle of adsorption and the ability of certain materials to remove dissolved substances from water have long been known. For about 100 years, adsorption technology has been used to a broader extent for water treatment, and during this time, it has not lost its relevance. Adsorption is a phase transfer process that is widely used in practice to remove substances from fluid phases (gases or liquid). It can also be observed as natural process in different environmental compartments. Adsorption is the phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (*Puri et al., 2010*).

The most general definition describes adsorption as an enrichment of chemical species from fluid phase on the surface of a liquid or a solid. In water treatment, adsorption has been proved as an efficient removal process for a multiplicity of solutes. Here, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces (*Eckhard, 2012*).

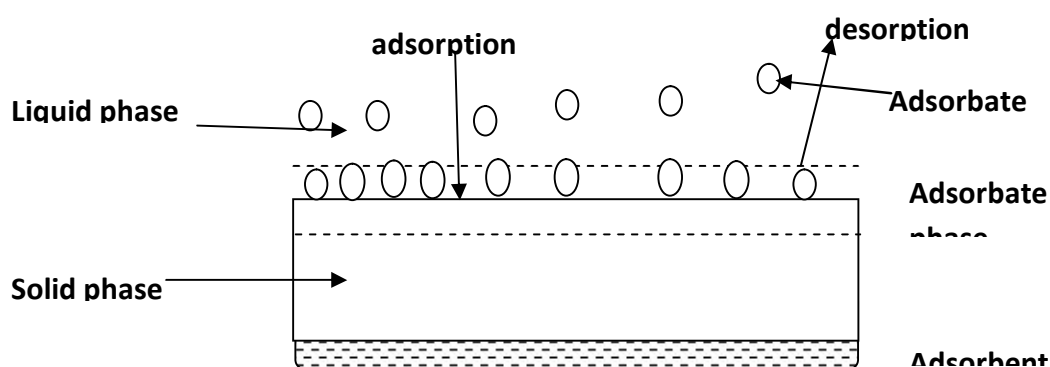


Figure (5): Basic terms of adsorption

2.9.3.1 Types of adsorption:-

(a) Physical Adsorption (Physisorption)

The adsorption induced by Van der Waals forces in which inter molecules attractions take place between favorable energy sites. Physisorption is independent of the electronic properties of the adsorbate and adsorbent molecules exchange of electrons does not occur in it.

The adsorbate is attached to the surface by relatively weak Vander Waals forces. In physisorption, multiple layers may be formed which have similar heats of adsorption and it is pre dominate at temperatures below 150° C and is characterized by a relatively low adsorption energy at most few kcal mol^{-1} .

(b) Chemical Adsorption (Chemisorptions):-

In this type the adsorbate undergoes chemical interaction with the adsorbent. Chemisorption involves an exchange of electrons between specific surface sites and solute molecules, a chemical bond being formed. Chemically adsorbed adsorbates are not free to move on the surface or within the interface. Chemical adsorption is characterized by high adsorption energy, since the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemisorption is more predominant at high temperatures compared to physisorption. Generally, only a single molecular layer can be chemically adsorbed.

2.9.3.2 Factors influencing adsorption:-

(i) Surface area of adsorbent:-

Adsorption being a surface phenomenon, the extent of it is generally considered to be proportional to the specific surface area (*Arun & Bahi, 1995*). Specific surface area is that proportion of the total surface area which is available for adsorption. The more finely divided and more porous adsorbents would be expected to yield more adsorption per unit weight of adsorbent.

(ii) Physical and chemical characteristics of the adsorbate:-

In general, the adsorbability of a compound increases with increasing molecular weight and increasing number of functional groups such as double bonds or halogens.

The solubility of the solute is also of primary concern for adsorption. There is an inverse relationship between the extent of adsorption of a particular solute and its solubility in the solvent from which the adsorption occurs.

Polarity of the adsorbate is another important factor.

A polar solute is preferably adsorbed by a polar adsorbent whereas a non-polar solute is more easily adsorbed by a non-polar adsorbent.

(iii) pH:-

Organic molecules form negative ions at high pH values, positive ions at low pH values, and neutral molecules at intermediate pH values. Adsorption of most organic materials is higher at neutral condition. In general, liquid phase adsorption of organic pollutants by activated carbon is increased with decreasing pH.

(iv) Temperature:-

The extent of adsorption should increase with decreasing temperature because the adsorption reactions are exothermic. However, increased temperature also increases the rate of diffusion of the solute through the liquid to the adsorption sites.

2.9.3.3 Adsorption isotherms:-

The rate of which a surface is covered with adsorbate depends on a number of factors.

One, as we have seen, is the activation energy; but as this is generally small or zero it rarely plays a dominant role. Another factor is the frequency of collisions, but this is very great under normal condition, and becomes slow on the time-scale of normal experiments only (*Atkins, 1978*).

Adsorption is usually described through isotherms that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption. Namely: Freundlich isotherm, Langmuir isotherm, BET isotherm ...etc.

(a) Langmuir isotherm:-

In 1916, Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

- 1- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- 2- Adsorbed molecules do not inter act.
- 3- All adsorption occurs through the same mechanism.

4- At the maximum adsorption, only a mono-layer is formed.
 Graphical of Langmuir isotherm has the form as in figure (2.3).

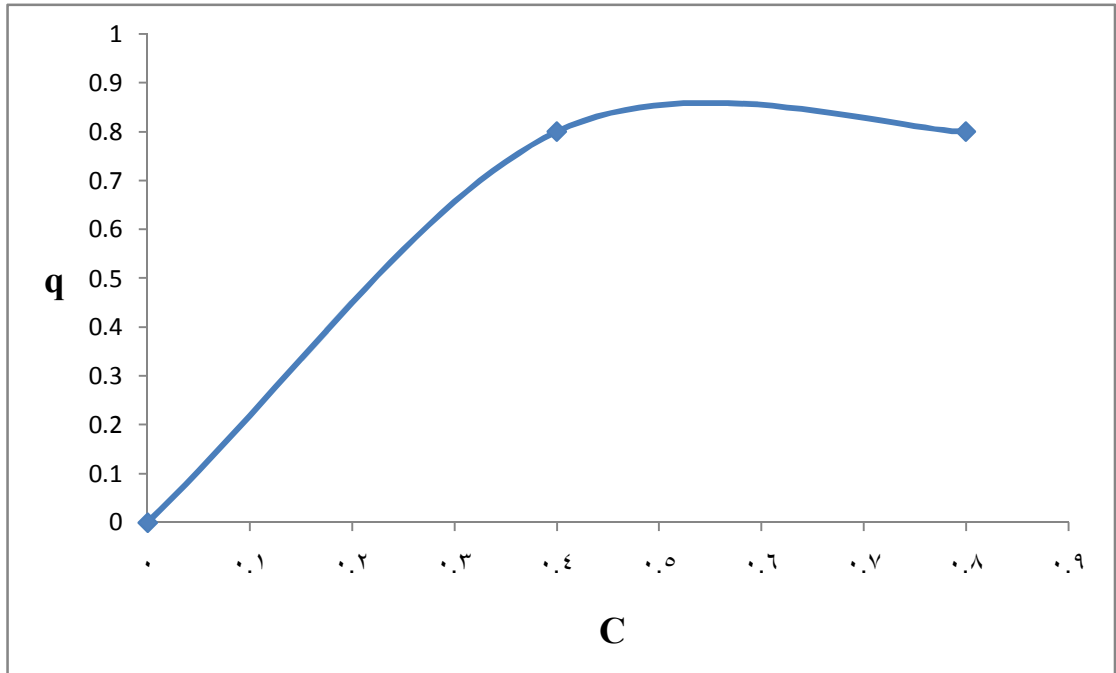


Figure (6): The Langmuir isotherm

Where:

q: The number of moles of solute adsorbed per unit weight of adsorbent.

C: Is the measured concentration at equilibrium.

The equation of Langmuir adsorption isotherm may be written as:

$$\Theta = \frac{K P_A}{1 + K P_A}$$

Where:-

K= the equilibrium constant

P= pressure of the adsorbate.

(a) EBT isotherm:-

Another milestone towards development of the adsorption science was the multilayer isotherm equation proposed by Brunauer et al. in 1938. The

multilayer adsorption theory was preceded by two significant papers by Brunauer and Emmett which appeared in 1935 and 1937. In the BET theory, it's assumed that the solid surface possesses uniform, localized sites and that adsorption at one site does not affect adsorption at neighboring sites, as was assumed in the Langmuir theory.

Graphically BET isotherm has the form as in figure (2.4).

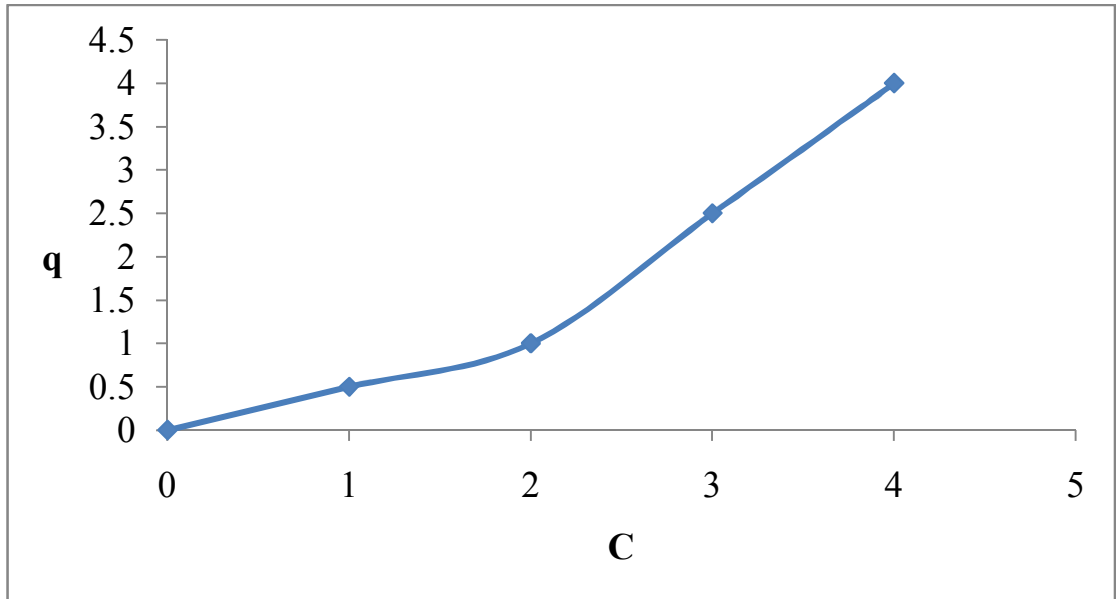


Fig (7): The BET isotherm

The BET equation:-

$$C/(C_s - C)q_e = 1/k_s q_m + [K_s - 1/K_s q_m] C/C_s$$

Where:-

q_e = The number of mole of solute adsorbed per unit weight at concentration.

C_s = The saturation concentration of the solute.

C = The measured concentration at equilibrium.

q_m = Number of mole of solute adsorbed per unit weight of adsorbent for complete one layer.

K_s = Constant expressing the energy.

A plot of $C/(C_s-C)q_e$ vs C/C_s give straight line of slop $(k_s-1)/k_s q_m$ and intercept $1/k_s q_m$.

(b) Freundlich isotherm:-

The Freundlich equation has been widely used for many years. This equation is special case for heterogeneous surface energies. The Freundlich equation has the general form:-

$$q_e = k_f c^{1/n}$$

Where:-

K and n= are constant, and $n > 1$

The equation can be rearranged to give:

$$\log q_e = \log k_f + 1/n \log c$$

Accordingly, a plot of $\log q$ vs $\log C$ should produce a straight line with $(1/n)$ slop, and $(\log k_f)$ intercept:-

Chapter Three

Materials and Methods

3. Materials and methods

3.1 Materials:

Rhamnus (Nabag) shells were collected as a waste after the outer sweet part of it was eaten.

3.2 Chemicals

Distilled water.

Sulfuric acid, H_2SO_4 , BDH, England.

Nitric acid, HNO_3 .

Cadmium nitrate $\text{Cd}(\text{NO}_3)_2$

3.3 Instruments

- Atomic Absorption Spectrometer, Shimadzu, Japan.
- HY-6 Man oeuvre style vibrator
- Analytical balance,
- Furnace,

3.4 Glassware & plastic ware:

Beakers, Volumetric flasks, Conical flasks, Pipette, Measuring cylinder, Glass rod, pp bottles.

All glassware were cleaned with soap and nitric acid then rinsed with distilled water.

3.5 Preparation of solutions:

3.5.1 Preparation of 5% (V/V) nitric acid:

A stock solution of 5% nitric acid was prepared by diluting 5.0 ml concentrated acid with distilled water and the volume was completed to 100 ml in a volumetric flask.

3.5.2 Preparation of 500 ppm cadmium ion solution

A stock solution of 500 ppm cadmium ion solution was prepared by dissolving 2.46 g of $\text{Cd}(\text{NO}_3)_2$ in distilled water and the volume was completed to 1000 ml in a volumetric flask. A series of concentrations 25, 50, 100 and 200 ppm were prepared by dilution using the stock solution.

3.6 Preparation of activated carbon from Rhamnus shells using sulphuric acid:-

50.00 g of Rhamnus (Nabag) shells were washed with distilled water and dried in an air for three hours. 100 cm³ of sulfuric acid (1:1) were added to the dried shells for 24 hours (pregnation). The content was filtered and left to dry in the air. The dried product was transferred to stainless steel tube and carbonization step was carried out at 600°C for 3 hours. Then the furnace was turned off and left to cool down gradually till room temperature. The activated carbon produced was collected, weighed and kept in a closed container. Part of product was analyzed by FT-IR and the other part was used for removal of heavy metals. The results were recorded in table (4.1).

3.7 Preparation of activated carbon from Rhamnus shells without sulphuric acid

50.00 g of Rhamnus (Nabag) shells were washed with distilled water and dried in an air for three hours. The dried product was transferred to stainless steel tube and carbonization step was carried out at 600°C for 3 hours. Then the furnace was turned off and left to cool down gradually till room temperature. The activated carbon produced was collected, weighed and kept in a closed container. Part of product was analyzed by FT-IR and the other part was used for removal of heavy metals. The results were recorded in table (4.2).

3.8 Analysis of activated carbon by FT-IR

The FT-IR was used to determine the functional groups present in the region between 310 to 4000 cm⁻¹. Small portion of a dried sample of activated carbon prepared with acid was mixed with KBr in a mortar using a pestle. This mixture was

used to prepare a thin disc and analyzed by FT-IR. The same method was repeated for the activated carbon prepared without acid. The results were recorded in table (4.3) & (4.4).

3.9 Equilibrium time for adsorption of cadmium metal ions by PAC

25.00 ml of cadmium ions solution at 50 ppm concentration were added to 0.25g activated carbon in five different plastic tubes at room temperature. Each tube was shaken for different time 10, 20, 30, 60 and 90 minutes. All samples were filtered and 1.0 cm³ from each solution was diluted to 25cm³ in a volumetric flask containing 1cm³ nitric acid (5%). Then the samples were analyzed for the metal content by atomic absorption. The same procedure was repeated by using activated carbon prepared with acid. The results were recorded in table (4.5) & (4.6).

3.10 The effect of metal ion concentration on adsorption:-

25.00 ml of cadmium ions solution at different concentrations 25, 50, 100 and 200 ppm were added to 0.25g activated carbon in four different plastic tubes at room temperature. All these tubes were shaken for 30 minutes then filtered. 1.0 cm³ from each solution was diluted to 25cm³ in a volumetric flask containing 1cm³ of 5% nitric acid. Then the samples were analyzed for the metal content by atomic absorption. The same procedure was repeated by using activated carbon prepared with acid. The results were recorded in table (4.7) & (4.8).

Chapter Four

Results and Discussion

4. Results and discussion

4.1 Preparation of activated carbon (AC):-

Tables (4.1) and (4.2) summarize the percentage yield for the activated carbon prepared using sulphuric acid and without acid. The yield of activated carbon when using sulphuric acid was found to be 32.31%. The yield of granular activated carbon without acid was found to be 24.88%. These results are lower than the yield reported for activated carbon prepared from nuts shell and softwood (40% – 45%), coal (70% - 85%) and coconut which gave around 45% (Nurul, 2007).

Table (4.1):

A) Preparation of activated carbon (AC) using sulphuric acid at 600 °C:-

Weight of (Nabag) shells /g	Weight of activated carbon /g	% Percentage of activated carbon
50.042	16.1692	32.31

Table (4.2):

B) Preparation of AC prepared without acid at 600°c :-

Weight of (Nabag) shells /g	Weight of activated carbon /g	% Percentage of activated carbon
50.0420	12.4513	24.77

4.2 Fourier transforms infrared (FTIR) spectroscopy for activated carbon AC:-

The results of FT-IR spectra of AC were presented in tables (4.3) & (4.4) and figures (1) and (2). The assignment for the main FT-IR band is for the AC prepared with and without acid respectively. From these results we observe the following:

For the AC prepared with acid the band at 3026cm^{-1} is due to the absorption of water molecules as a result of an O-H stretching mode of hydroxyl group and adsorbed water, while the band at 2800cm^{-1} is attributed to C-H interaction with the surface of the carbon. The sharp band at 1139 cm^{-1} is due to Si-O-C stretching vibration. The band at 871cm^{-1} is due to Si-H deformation.

For the AC prepared without acid the band 3174cm^{-1} is due to the absorption of water molecules as a result of an O-H stretching mode of hydroxyl group and adsorbed water, while the band at 2877cm^{-1} is attributed to C-H interaction with the surface of the carbon (Al Qodah, 2009). The band 817cm^{-1} refers to Si-H deformation. The band in 495cm^{-1} is Si-O bending.

Table (4.3):

The main FT-IR band for the AC prepared with acid:

Band position (cm^{-1})	Activated carbon with acid
3026	O-H stretching vibration
2800	C-H stretching vibration
1139	Si-O-C stretching vibration
871	Si-H deformation

Table (4.4):

The main FT-IR band for the AC prepared without acid:

Band position(cm^{-1})	Activated carbon without acid
3174	O-H stretching vibration
2877	C-H stretching vibration
817	Si-H
495	Si-O bending

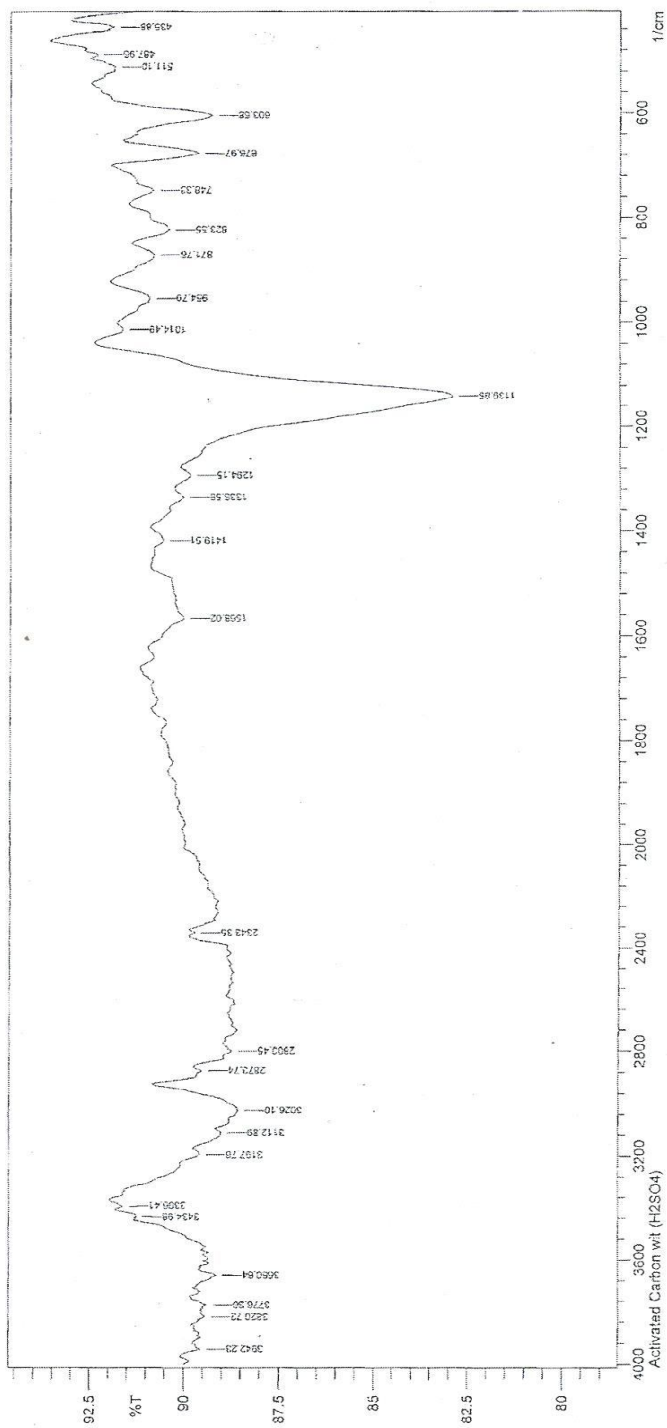


Fig (8): FT- IR spectrum for activated carbon prepared with acid

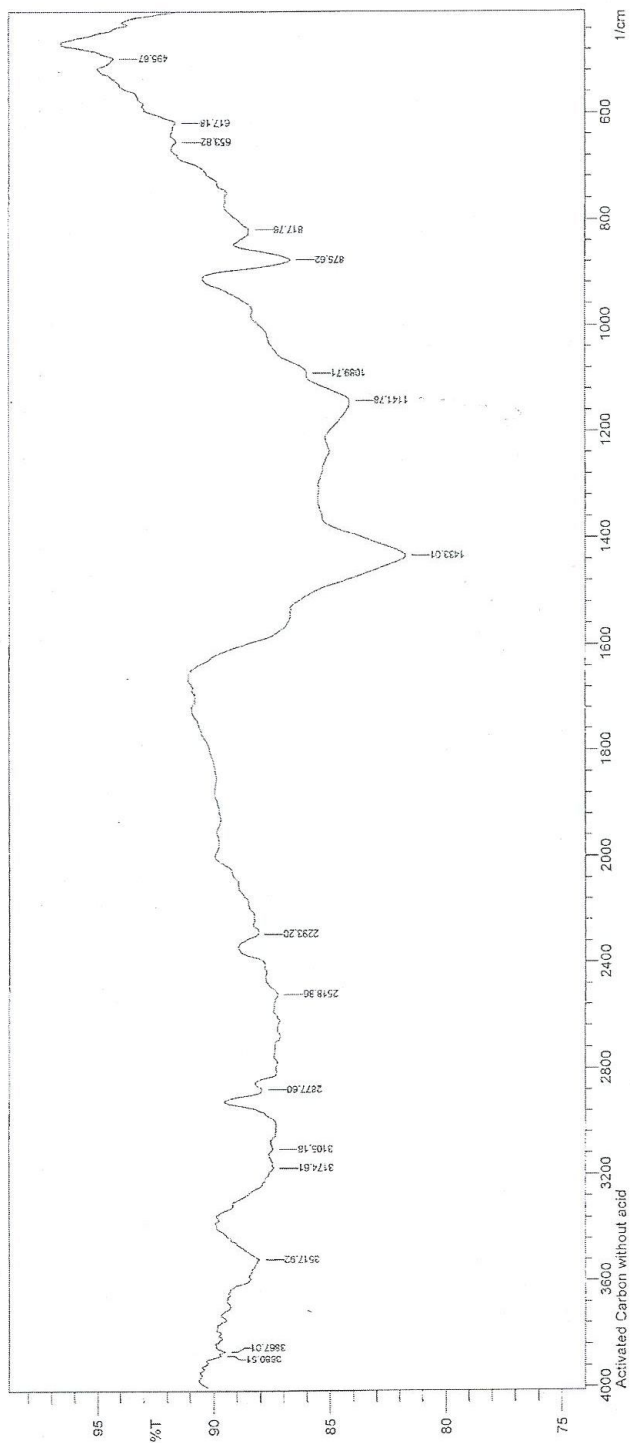


Fig (9): FT- IR spectrum for activated carbon prepared without acid

4.3 Removal of cadmium ion from water by using powder activated carbon (PAC):

Table (4.5) and Figure (3) show the equilibrium time for adsorption of cadmium ions using PAC prepared with acid. The equilibrium time for adsorption of Cd^{+2} ions on PAC was found to be increased with the increasing time. These results are lower than the results reported for the percentage removal of activated carbon prepared from other materials like coconut and others. This may be attributed to the low absorptive capacity of this type of carbon. The low percentage removal in this case also may be due to the presence of some traces of remaining acid that lower down the pH of the medium. It is know that the adsorption decreases with the decrease in pH.

Table (4.6) and Figure (4) show the equilibrium time for adsorption of cadmium ions using PAC prepared without acid. The maximum adsorption of Cd^{+2} on PAC was given after 10 minutes shaking. Then lowered after 20 minutes and started to increase with time after that till 90 minutes the end of shaking the solution with PAC. These results are lower than the results reported for the percentage removal of activated carbon prepared from other materials like coconut and others, but it is better than the results of percentage removal of PAC prepared with acid. This may be attributed to the low absorptive capacity of this type of carbon.

Table (4.5)

A) Equilibrium time for adsorption of cadmium using PAC prepared with acid

Container No.	Time/Sec	Initial concentration of cadmium (C_0) ppm	Concentration of cadmium after adsorption (C_t) ppm	Cadmium removed $C_0 - C_t$	% Removal
A1	10	1.9411	1.8281	0.113	5.82%
A2	20	1.9411	1.7770	0.6141	8.45%
A3	30	1.9411	1.9250	0.0161	0.82%
A4	60	1.9411	1.8254	0.1157	5.96%
A5	90	1.9411	1.7097	0.2314	11.92%

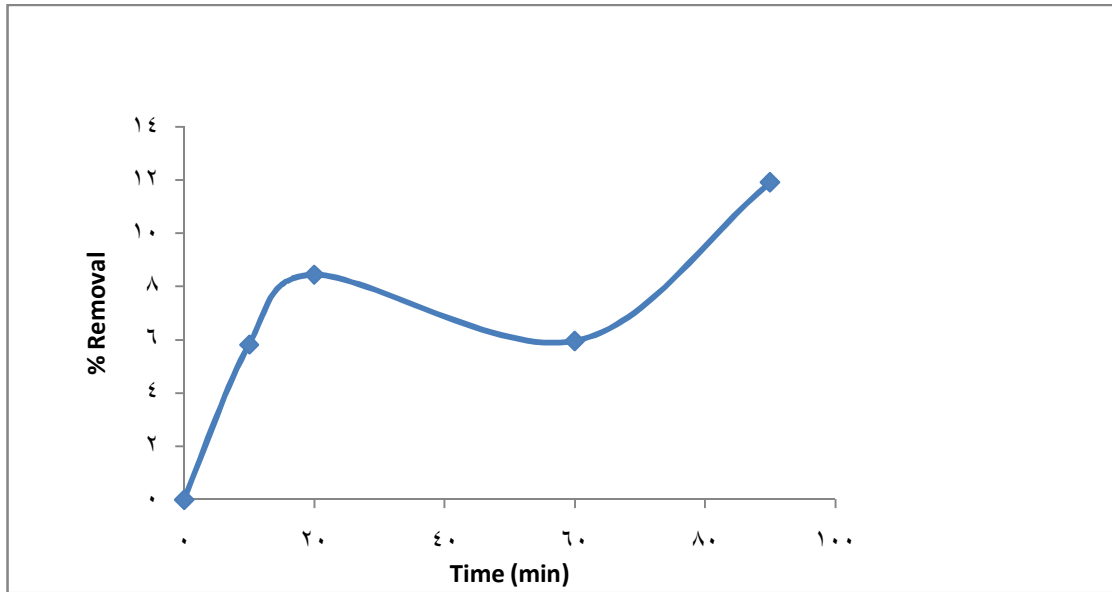


Figure (10): Equilibrium time for adsorption of cadmium using PAC prepared with acid

Table (4.6):

B) Equilibrium time for adsorption of cadmium using PAC prepared without acid

Container No.	Time /Sec	Initial concentration of cadmium (C_0) /ppm	Concentration of cadmium after adsorption (C_t) / ppm	Cadmium removed $C_0 - C_t$	% Removal
A6	10	1.9411	1.3841	0.557	28.69%
A7	20	1.9411	1,4998	0.4413	22.73%
A8	30	1.9411	1.4218	0.5193	26.75%
A9	60	1.9411	1,3976	0.5435	27.99%
A10	90	1.9411	1.3922	0.5489	28.72%

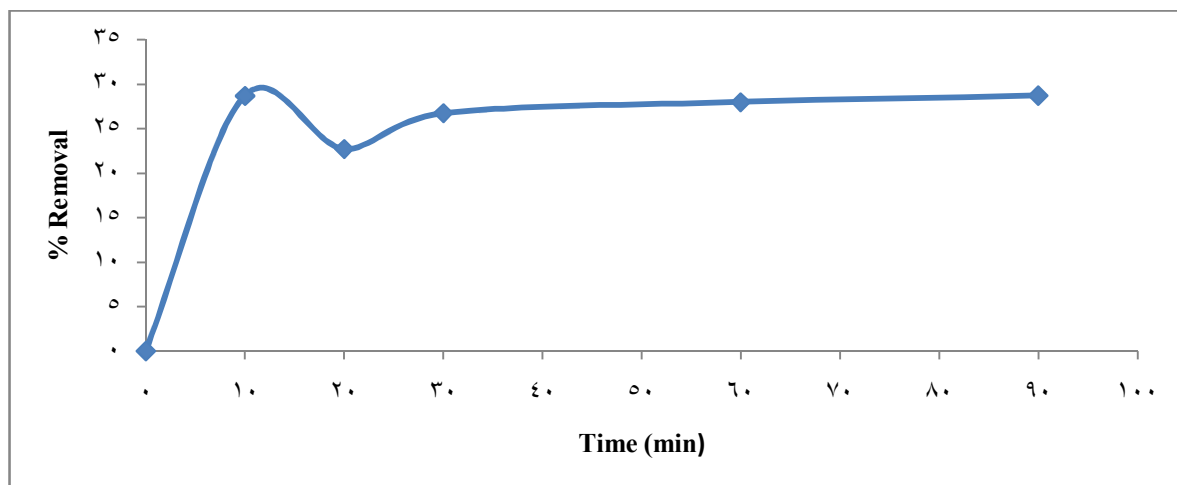


Figure (11): Equilibrium time for adsorption of cadmium using PAC prepared without acid

4.4 The effect of concentration on percentage removal of cadmium ion with AC at constant time

Table (4.7) and figure (5) show the percentage removal of cadmium ion with AC prepared without acid at different concentrations. Table (4.8) and figure (6) show the percentage removal of cadmium ion with AC prepared with acid at different concentrations. It was found that the percentage removal decreased as the concentration of Cd^{+2} in the solution increased in both carbons. The highest percentage removal of Cd^{+2} by the two types of carbons was obtained at 1.002ppm. In general the results showed that AC prepared without acid gave higher percentage removal than AC prepared with acid. The results showed that in both activated carbons the percentage removal of Cd^{+2} is high when the concentration is low and when the concentration of Cd^{+2} increased the percentage removal decreased. These results agreed with the results obtained by *Baskaran et al, 2011*.

Table (4.7):

The effect of concentration on removal of cadmium with PAC prepared without acid at constant time

Container No.	Time /Sec	Initial concentration of cadmium(C_0) / ppm	Concentration of cadmium after adsorption (C_t) / ppm	Cadmium removed $C_0 - C_t$	% Removal
B1	30	1.0020	0.4989	0.5031	50.20%
B2	30	1.9411	1.3007	0.6404	32.99%
B3	30	3.8004	3.1466	0.6538	17.20%
B4	30	6.9405	6.2624	0.6781	9.77%

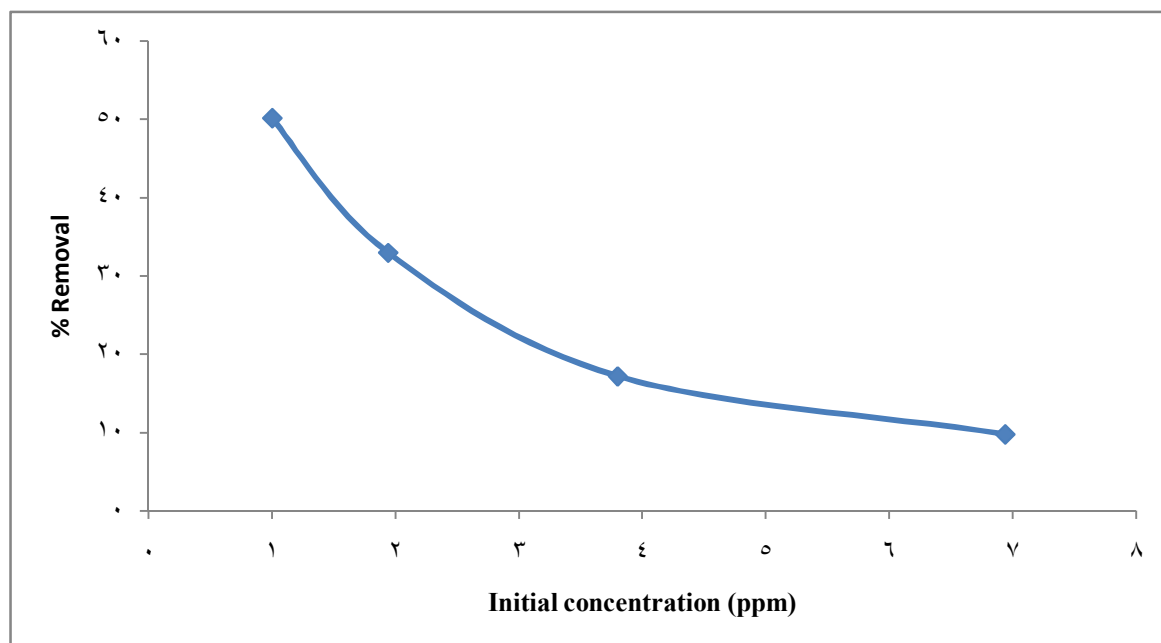


Figure (12): The effect of concentration on removal of cadmium with PAC prepared without acid at constant time

Table (4.8):

The effect of concentration on removal of cadmium with PAC prepared with acid at constant time

Container No.	Time /Sec	Initial concentration of cadmium(C_0) /ppm	Concentration of cadmium adsorption (C_t) /ppm	Cadmium removed $C_0 - C_t$	% Removal
C1	30	1.002	0.8540	0.148	14.77%
C2	30	1.9411	1.6559	0.2852	14.69%
C3	30	3.8004	3.5421	0.2583	6.79%
C4	30	6.9405	6.9082	0.0323	0.46%

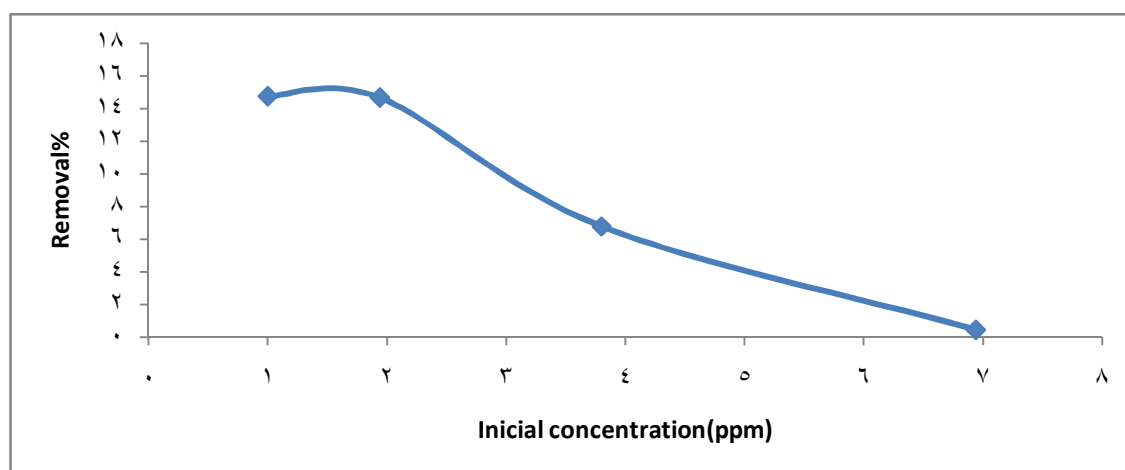


Figure (13): The effect of concentration on removal of cadmium with PAC prepared with acid at constant time

Chapter Five

Conclusion and Recommendation

5.0 Conclusion & recommendation

5.1 Conclusion:

The results obtained indicate that, the percentage yield for the carbon prepared using sulfuric acid was found to be 32.31% and for activated carbon prepared without acid was 24.88%. These results are lower than the results obtained when using AC furnace designed for production of AC.

The FT-IR analysis of Nabag shell's activated carbon shows the presence of OH, CH, Si-O and Si-H groups. These are the same functional groups found in all types of AC prepared from the different agricultural products

The equilibrium time for adsorption of cadmium ions on AC prepared with acid was reached in 20 minutes and 10 minutes for that prepared without acid.

The prepared activated carbons were used to remove cadmium ions from water using batch method. The percentage removal of cadmium ions from water was found to be decreased as the concentration of Cd^{2+} in the solution increased using both carbons. The activated carbon prepared without acid gave higher percentage removal than the activated carbon prepared with acid.

5.2 Recommendation:

- 1- The activated carbon can be prepared using the AC furnace designed for the carbonization in presence of CO_2 or N_2 or other gases.
- 2- Other chemicals such as ZnCl_2 , H_3PO_4 , NaOH or others can be attempted for pregation for seeking better surface area.
- 3- Further analysis by XRF, CEM and BET can be conducted for these carbons.
- 4- These activated carbons can be used for removal of other heavy metals ions or organic pollutants from water.
- 5- The column technique can be conducted to attempt another method of adsorption instead of batch method as this have many applications in the industry.
- 6- Kinetic and thermodynamics can be studied for the prepared ACs.

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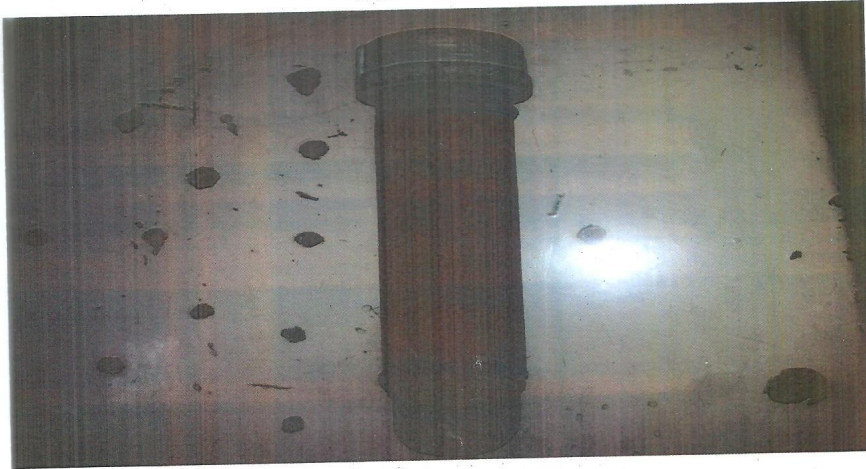
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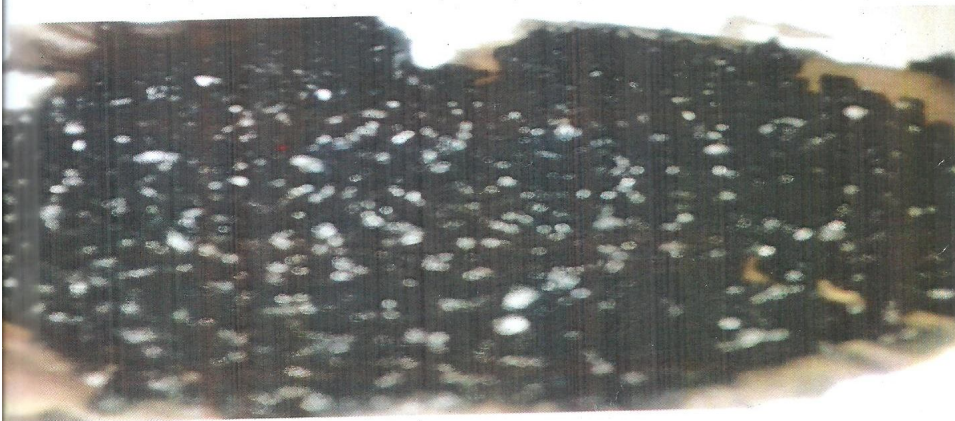
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Appendix (A)



The stainless tube



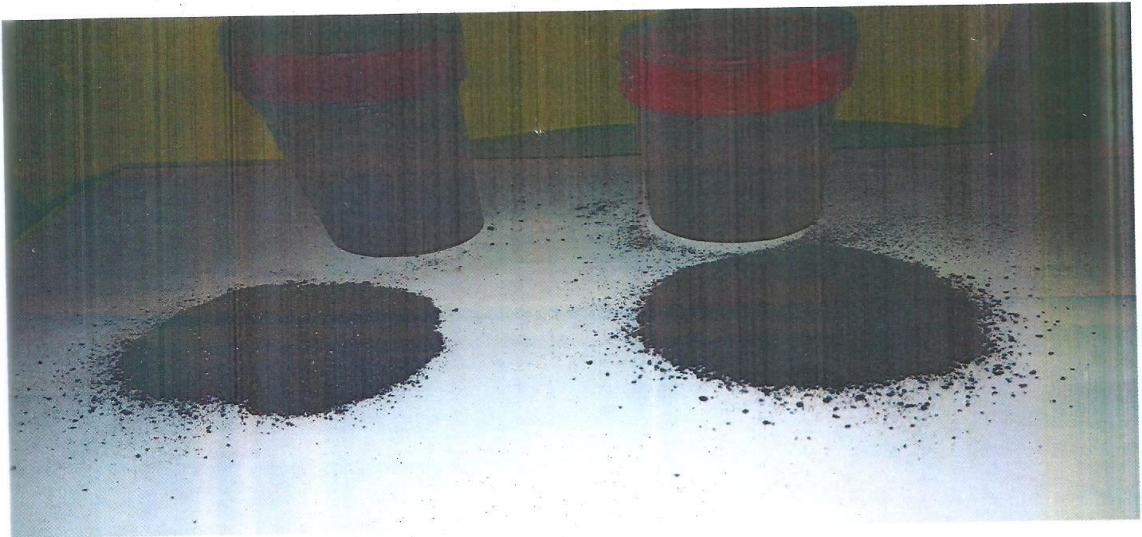
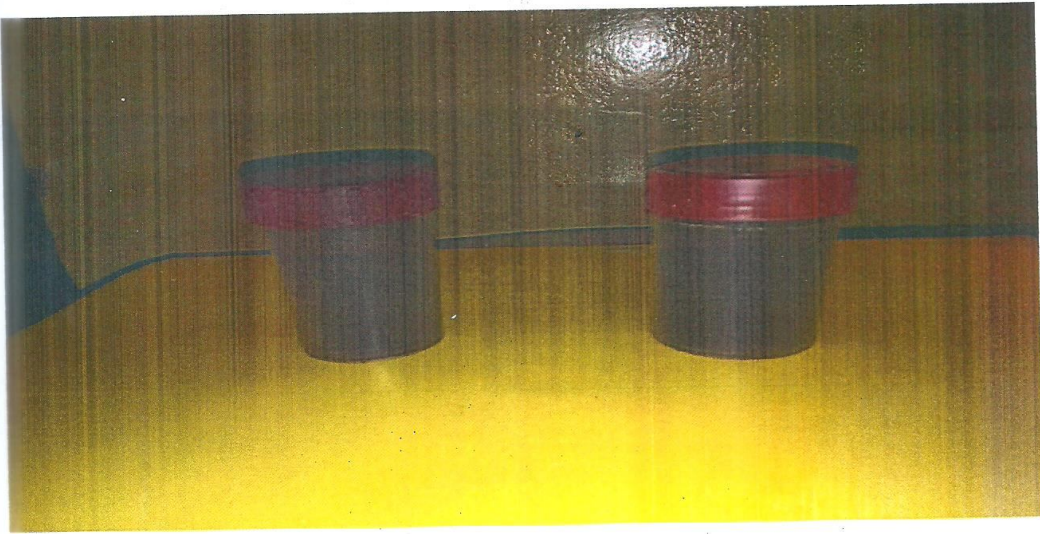
The Activated carbon



The oven



Analytical Balance



The Powder Activated carbon (PAC)