بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

SUNIVERSITY OF SCIENCE AND TECHNOLOGY

College of Graduate Studies

Preparation and applications of activated carbon from petroleum coke

تحضير وتطبيقات الكربون المنشط من الفحم البترولي

A thesis submitted in fulfillment of M.Sc. degree in Chemistry.

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Dedication

I dedicate this thesis to my parents who have always been my nearest and so closed to me that I found them whenever I needed, Siddig and Mawahib, It is their unconditional compassion and love that motivates me to set higher targets. I also dedicate this thesis to my wonderful brothers Mutaz,Mohammed,Amin and gorgeous sisters Susan, Sahar, Sulafa, Sara, and taiseer. Another dedication is for my friends with whom I share immortal memories.

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Abstract:

Samples of petroleum coke were used to prepare activated carbon (AC) using potassium hydroxide as active agent at 800 **C**. The results show that AC obtained has Iodine number (IN) and Methylene blue (MB) of 1242.40, 51.60 mg/g respectively. The AC has an adsorption capacity of 942 mg/g of dispersed oil at pH 4. The adsorption isotherm of oil fits Freundlich isotherm model with K, 1/n are (2.47) , (0.198) and an (R) of 0.9565. The adsorption capacity of Zinc (+2) is 368 mg/g. K, 1/n and R values are 1.25, 0.5122 and 0.971 respectively.

المستخلص:

أستخدمت عينات من الفحم البترولي لحضير الكربون المنشط بإستخدام هيدروكسيد البوتاسيوم كعامل تنشيط عند درجه حراره تنشيط 800 درجه مئويه. أوضحت النتائج أن رقم اليود والميثيل الأزرق للكربون المنشط هي 1242.40 و 51.6ملجم/جم . والقيمه الادمصاصيه 942 ملجم/جم بالنسبه الي البترول العالق في الماء عند رقم هيدروجين 4. منحني الإدمصاص للبترول المعلق في الماء يتوافق مع منحني فريندرلتش بقيم ثوابت K,1/n تساوي (0.198),(2.47) و خطاء (R) (0.9565)علي التوالي. القميه الادمصاصيه للزنك (+2) كانت (368) ملجم/جم.وقيم K,1/n و (R) كانت 1.25 , 0.5122 و 0.971 علي التوالي.

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Introduction

CHAPTER ONE

1.1: Activated carbon

Activated carbon is a solid, porous, black carbonaceous material; it is distinguished from elemental carbon by the absence of both impurities and an oxidized surface. It can be prepared from a large number of sources such as coconut, wood, peat, coal, tar, sawdust, and petroleum cokes (Mattson and Mark, 1971).

Any carbon source can be converted into activated carbon via a number of methods. Usually, the process is divided into carbonization and activation, during carbonization, most of the non-carbon elements are removed in gaseous form by the pyrolytic decomposition of the source material. The porous structure is mainly developed during activation by means of an activation agent that reacts with carbon.Such agents include acids, bases, and other substances in a stream of activating gases such as steam (H_2O), nitrogen (N_2) or carbon dioxide (CO_2) (Lambiotte, 1942).

1.2: Delayed petroleum coke

Delayed coking is a thermal cracking process used, in petroleum refineries to upgrade and convert petroleum residuum, bottoms from atmospheric and vacuum distillation of crude oil, into liquid and gas product streams leaving behind a solid concentrated carbon material (petroleum coke). A fired heater with horizontal tubes is used in the process to reach thermal cracking temperatures of 485 to 505**C** (905 to 941**F**). With short residence time in the furnace tubes, coking of the feed material is thereby “delayed” until it reaches large coking drums downstream of the heater. There are three physical structures of petroleum coke: shot, sponge, or needle coke can be produced by delayed coking. These physical structures and chemical properties of petroleum coke determines the end use of the material which can be burned as fuel, calcined for use in aluminum, chemical, steel industries, gasified to produce steam, electricity, or gas feedstocks for the petrochemicals industry (Arthur,1998).

1.3: Produced water:

In subsurface formations, naturally occurring, rocks are generally permeated with fluids such as water, oil, or gas or some combination of these fluids. It is believed that, in most oil-bearing formations rocks are completely saturated with water prior to the invasion and trapping of petroleum. The less dense hydrocarbons migrate to trap locations, displacing some of the water from the formation in becoming hydrocarbon reservoirs. Thus, reservoir rocks normally contain, both petroleum hydrocarbons liquids and gas and water. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities (Amyx*et al*, 1960).

Produced water is present in a reservoir with the hydrocarbon resource and is produced with crude oil or natural gas. When hydrocarbons are produced, they are brought to the surface as a produced fluid mixture. The composition of this produced fluid depends on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, (produced solids) such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities (Veil, 2004).

1.4: Objectives of this study are:

- To prepare activated carbon (AC) from petroleum.
- To study adsorption characteristics of activated carbon (AC).
- To use prepared activated carbon (AC) to remove pollutants from produced water from petroleum production activities, thus reduce the environmental impact of organic and inorganic pollutants from petroleum industry.

CHAPTER TWO

2:Literature review

2.1:Activated Carbon production

2.1.1: activated carbon characteristics

Activated carbons are carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces(Mattson, 1979). The slit-shaped model ,Fig 2.1, represents the microstructure of activated carbon (AC) (Stoeckli, 1990).

The most important property of activated carbon (AC) is the pores structurethat determines its usage. The total number of pores, their shape and size determine the adsorption capacity and the dynamic adsorption rate of the activated carbon. IUPAC classifies of porous materials include the following classes;

macropores: $d > 50nm$
mesopores: $2 \leq d \leq 50nm$
micropores: $d < 2nm$
supermicropores: $0.7 < d < 2nm$

Whered is the pore width for slit type pores or the pore diameter for cylindrical pores.Fig.2.2 illustrates the different types of pores (Rodriguez and Linares., 1989).

The macropores act as transport pathways, through which the adsorptive molecules travel to the mesopores, from where they finally enter the micropores. The micropores usually constitute the largest proportion of the internal surface of activated carbon (AC) and contribute most to the total pore volume. Most of gaseous adsorption takes place within these micropores, where attractive forces are enhancedand the pressures. Thus, the total pore volume and the pore size distribution determine the adsorption capacity.

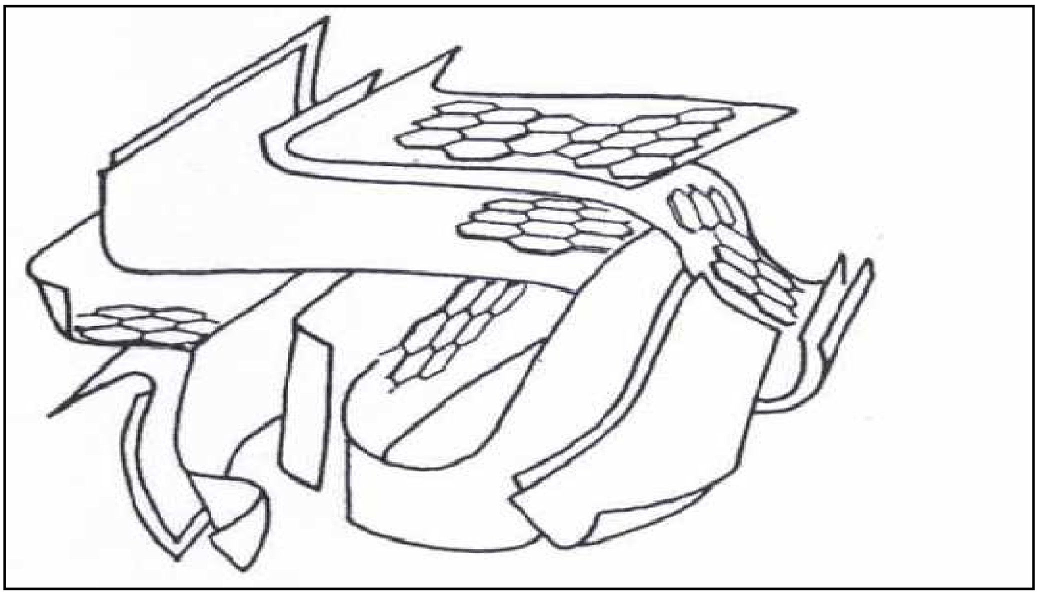

Fig.2.1: A schematic representation of the structure of activated carbon (AC).

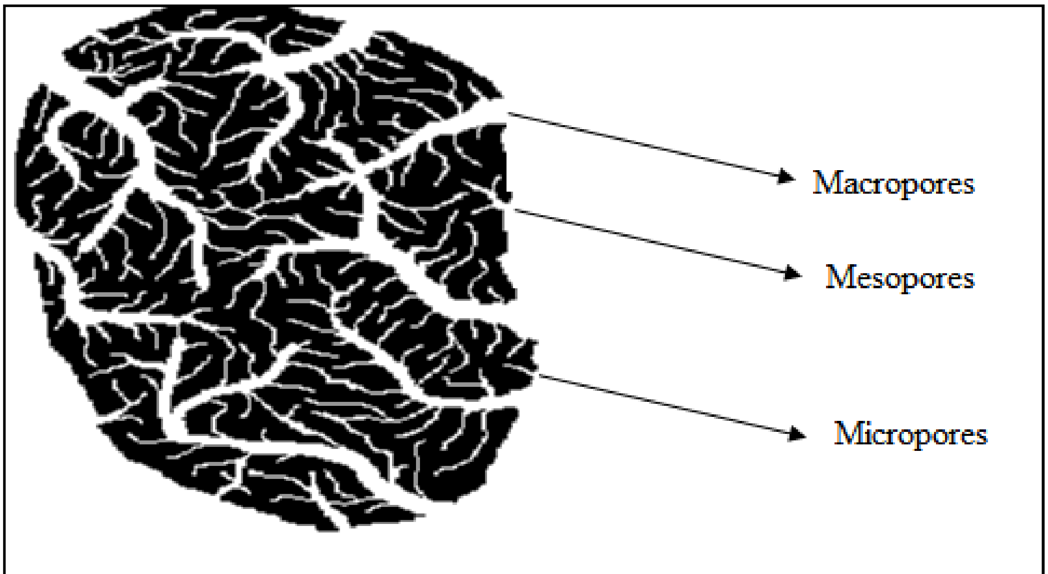

Fig.2.2: Types of pores in an activated carbon (AC)particle.

Carbon atoms located at the edges of the basal planes are unsaturated carbon atoms, which possess unpaired electrons, these sites are, usually, bonded to heteroatoms giving rise to surface groups. Among these groups, oxygen-containing surface groups are by far the most common in carbon. In particular, activated carbons have a relatively large edge area, which results in a strong propensity for oxygen chemisorptions. Thus, molecular oxygen can dissociate into atoms that react chemically with atoms of carbon to form oxygen surface compounds. This oxidation process is particularly significant as the temperature of the reaction increases, but also at room temperature for carbons, previously, treated at high temperature, which results in a highly reactive surface. Oxygen-containing surface groups are not only formed by reaction with oxygen but also can result from reaction with many other oxidizing gases such as ozone, nitrous oxide, carbon dioxide,etc. and with oxidizing solutions like nitric acid, hydrogen peroxide,etc. thus, the surface chemistry of activated carbon (AC)can be tailored by oxidation with different agents in order to create oxygen functionalities or by heat treatment in order to remove them either selectively or completely depending on the temperature used. Fig. 2.3 summarizes the most important surface groups that may be present on activated carbon (AC) surfaces (Teresa *et al*., 2006).

The dynamics of adsorption in a packed activated carbon (AC) bed is influenced by the shape and size of activated carbon (AC) particles and their effect on the flow characteristics. The smaller activated carbon (AC)particle is the better the access to its surface area and the faster the rate of adsorption.The porous structure is mainly developed during activation by means of an activation agent that reacts with carbon. Such agents include synthetic acids, bases, and other substances in a stream of activating gases such as steam (H_2O), nitrogen (N_2) or carbon dioxide (CO_2)(Sing *et al.*, 1985).

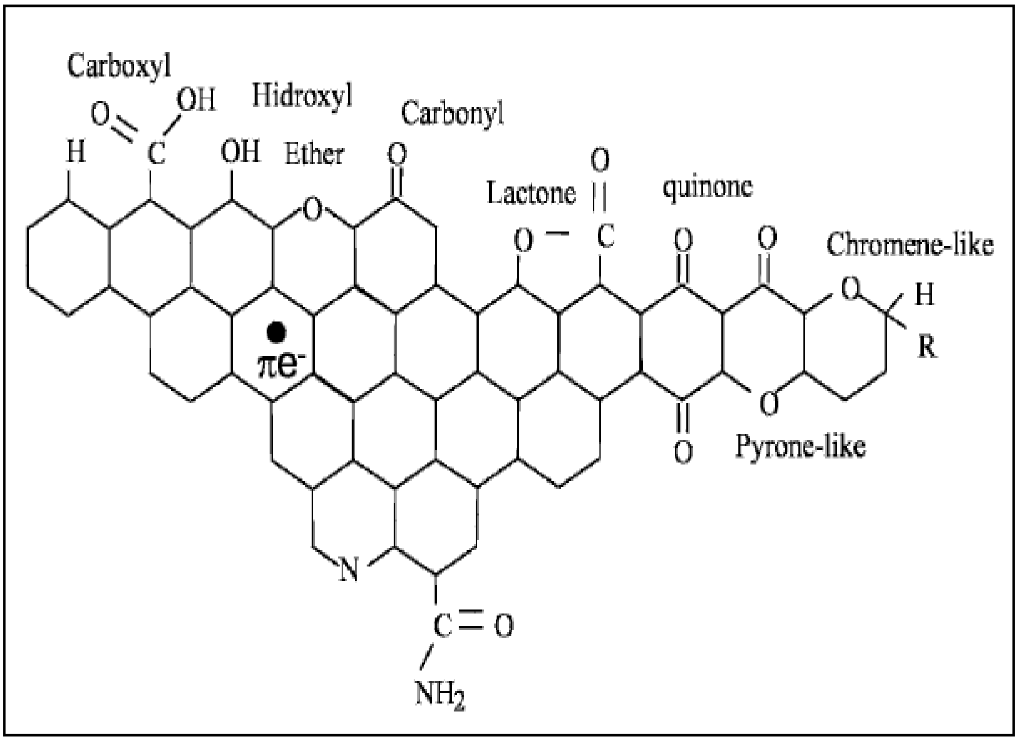

Fig.2.3:Surface groups that may be found on activated carbon (AC).

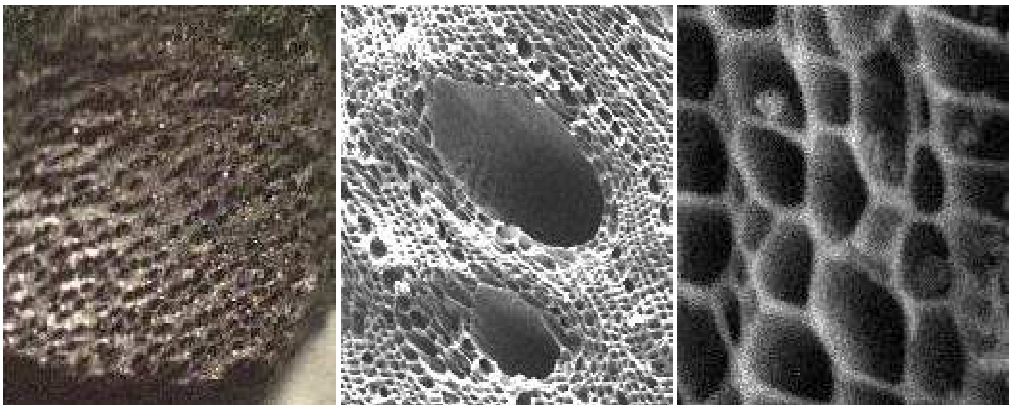

Fig.2.4: SEM of activated carbon (AC).

Activated carbon (AC) is characterized by its, extraordinary, large specific surface areas, well-developed porosity and tunable surface-containing functional groups (Baker.,1992). It is widely used as adsorbent for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater (El-Hendawy*et al*.,2003). The surface oxygen functional groups can be, easily, introduced by different activation methods including dry and wet oxidizing agents. Dry oxidation methods involve the reaction with hot oxidizing gas such as steam and CO_2 at temperatures above 700 **C** (Smisek*et al*., 1970). Wet oxidation methods involve the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid (H_3PO_4), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), zinc chloride ($ZnCl_2$) potassium permanganate ($KMnO_4$), ammonium persulphate ($(NH_4)_2SO_8$), potassium hydroxide KOH, etc. From the above oxidizing agents, phosphoric acid and zinc chloride are usually used for the activation of lignocellulosic materials, which have not been carbonized before (Puziy., 2002). On the other hand, potassium hydroxide is usually used to activate coal or chars precursors. It has been reported that zinc chloride produces activated carbon with higher specific area than that produced using phosphoric acid (Thomas *et al*., 1997). However, phosphoric acid activation is widely preferred over zinc chloride because $ZnCl_2$ has bad environmental impact and cannot be used in the food and pharmaceutical industries (Srinivasakanna, 2006). Activated carbon usually increases the cost of the treatment process. Its economical drawback hasstimulated the interest to utilize cheaper raw materials for the production of activated carbon (Rengarag*et al*., 2002).

A wide variety of agricultural by-products and wastes has been investigated as cellulosic precursors for the production of ACs in addition to hard wood and bituminous coal. These precursors include coconut shell and wood (Laine*et al.,* 1989), Olive stones(Rodriguez *et al.,* 2001),(Lafi*et al*.,2001), sugarcane bagasse (Elsheikh e*t al*.,2003) pecan shells(Rengarag*et al*.,2002), palm seed(Garcia *et al*.,2003), apple pulp(Rengarag*et al*.,1996) rubber seeds(Legrouri*et al*.,2005) andmolasses(Khalili*et al*., 2000). Commercial ACs are commonly produced from naturally occurring carbonaceous materials such as coal, wood and peat (Rozada*et al*.,2003). Due to the growing need for activated carbons in our society and the high cost of raw materials , many researchers have attempted various wastes such as tires(Mui.,2004), resins(Yue.,2006), agricultural byproducts (Lee *et al*., 2003; Cha´ vez*et al*., 2008; Kalderis*et al*., 2008) and dried sewage sludge(Zhang et al., 2005;Rio et al., 2006)as raw materials and proposed new production methods (Mene´ ndez*et al*., 2005; Wang *et al*., 2008) for activated carbons with potential applications in pollution control. Furthermore, more interest has been devoted to utilize some wastes of carbonaceous materials such as paper mill sludge (Khalili*et al*.,2008), old newspapers (Otowa*et al*.,1990) and waste tires (Rozada*et al*.,2005). Recently, activated sludge has been produced as a result of wastewater treatment activities and has emerged as an interesting option for the production of activated carbon (Jeyaseelan*et al*.,1999; Tay*et al*.,2001) The results reported in these studies indicate that chemical activation of the sewage sludge with $ZnCl_2$ and H_2SO_4 produced activated carbon of high adsorption capacity comparable with that of commercial activated carbon. In addition, the choice of a cheap precursor for the production of activated carbon means both considerable savings in the production cost and a way of making use of a waste material, thus reducing its disposal problem (Rozada*et al*.,2003).

Activated carbons (AC) are increasingly used as an economic and stable mass separation agent for the removal of surfactants to raise the final product quality in many industrial processes. Activated carbons also play an important role in many areas of modern science and technology such as purification of liquids and gases, separation of mixtures, and catalysis (Kenneth.,2002). Adsorption of activated carbon is governed by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic compounds (Bilal *et al.*,1996).

According to Torregrosa-Macia(Torregrosa*et al.*,1997), for a given industrial application, a solid adsorbent with a relatively wide pore size distribution can be obtained solely through a chemical activation process. Physical activation can further enhance the adsorbent‘s pore structure due to a partial oxidation of the carbonized material by gases such as CO/CO_2 or steam (Molina *et al.*, 1996).

Analysis of the surface physical properties of activated carbon (AC) includes determination of the total surface area, extent of microporosity, and characterization of the pore size distribution. Nitrogen adsorption isotherms are commonly used for these types of surface analyses (Carrott e*t al.*,1987; Mikhail .,1986; Harkins and Jura., 1943;Aranovich and M. Donohue.,1998). The measured relative pressure and adsorbed volume of nitrogen gas are commonly used in various mathematical models (i.e. BET model) to calculate the monolayer coverage of nitrogen adsorbed on the adsorbent surface, while the characteristics of the pore structure and pore distribution can be identified from comparative plots (Barret*et al.*,1951; Lippens and de Boer.,1965; Gregg and Sing.,1982). The extent of the microporosity is commonly evaluated by applying low-pressure isotherm data to the Dubinin–Radushkevich (DR) equation (Sing*et al.*,1985) the pore size distribution and the corresponding surface areas of the mesoporous adsorbents are traditionally calculated from the hysteresis loop according to the BJH theory, which is based on the Kelvin equation (Barret*et al*.,1951).

2.1.2: Manufacturing Activated Carbon

Production of activated carbon (AC) involves two processes, carbonization, followed by activation. Before carbonization and activation, the starting materials are adjusted to exhibit the desired final physical properties such as granule size, shape, roughness, and hardness. These properties are influenced by production techniques. Blends of the pulverized material and binders (sugar, tar, pitch, and lignin) are often used to obtain desired particle size during extrusion.Carbonization or pyrolysis consists of slow heating of the material at temperatures usuallybelow800ºCintheabsenceofair. During this stage of pyrolysis, volatile products are removed from the starting material. Carbonizationcansometimesbe controlled by addition of dehydrating agents such as zinc chloride or phosphoric acid, which are recovered for reuse. Activation consists of treating the pyrolized char with activating agents such as steam or carbon dioxide at elevated temperatures, 800-900ºC, that transforms the char into numerous pores which are systematically developed and enlarged, thus enabling the production of a well defined pore system in the activated carbons (Sing *et al.*,1985).

During activation, the surface area or adsorption is determined by

(1) The chemicalnatureandconcentration of theactivating agent,

(2) The temperature of the reaction,

(3) The extent to which the activationis conducted.

(4) Theamountandkind of mineral ingredients in the char.

Temperature must be high enough to provide a reasonably rapid rate of activation,buttemperaturesabove1000ºCareto be avoided because they begin to impair adsorption. Activation with steam or carbon dioxide is conducted at temperatures from 800º to 900ºC. Activation with air involves an exothermic reaction and measures must be taken to keep the temperature from rising above proper limits usuallynotover600ºC.

Other activation processes include the use of dolomite, sulfates, phosphoric acid, sodium and potassium hydroxides, thiocyanates, sulfide, and potassium and sodium carbonates (Hassler, 1963).

After activation, carbon intended for batch treatment of liquid systems is pulverized to a suitable size. Most activation processes produce a carbon with a pH >7 an alkaline, although some processes produce an acid carbon. The pH can be adjusted by supplementary addition of acid or alkali to meet the varied needs of different industrial users. When the intended use requires low ash content with low conductivity, the carbon is washed with water, or with acid and then with water. activated carbon (AC), is used in columns or beds for gas and vapor systems, and also for processinganumberofliquids. It must possess sufficient mechanical strength to withstand the abrasion incident to continued use. The development of high adsorptive power is accompanied by loss of mechanical strength and density. Therefore the activation stage can not be too short because the carbon would lack needed adsorptive power; conversely, it cannot betoo long for then the carbonwould be too soft and bulky(Molina *et al.*, 1996).

Few materials, in the natural state, can be converted into activated carbon with high density and low attrition. Less dense material, however, can be made dense and yield a hard carbon when mixed with a binder. The binder should be a substance which when carbonized does not liquefy or expand. However, some shrinkage is desirable. The tarryby-products from woods and certain grades of anthracite and bituminous coal have been found to be good binders. To be suitable as a binder, a substance should liquefy or soften during carbonization and swell sufficiently to give a porous structure. Suitable binders include sugars, tar, pitch, and lignin (Mingwang., 2004).

2.1.3 Classification of activated carbon

Activated carbons (AC) are complex products which are difficult to classify on the basis of theirbehavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics (Teresa J.,2006).

2.1.3.1: Powdered activated carbon (PAC)

PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve. Activated carbon (AC) is defined as the carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material. ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC, generally, added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters(Teresa J.,2006).

2.1.3.2: Granular activated carbon (GAC)

Granular activated carbon has a, relatively, larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapor phase applications. A 20×40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as 85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) generally specified as 95% retained(Teresa J.,2006).

2.1.3.3: Extruded activated carbon (EAC)

EAC combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content (Teresa J.,2006).

2.1.3.4: Impregnated carbon

Porous activated carbon (AC) containing several types of inorganic impregnate such as iodine, silver, cations such as Al, Mn, Zn, Fe, Li, Ca alsohave been prepared for specific application in air pollution control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purification of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and $Al(OH)_3$, a flocculating agent. Impregnated carbons are also used for the adsorption of H_2S and thiols. Adsorption rates for H_2S as high as 50% by weight have been reported (Teresa J.,2006).

2.1.3.5: Polymer coated carbon:

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion. Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood (Teresa J.,2006).

2.1.3.6: Others

Activated carbon is also available in special forms such as cloths and fibres. The "carbon cloth" for instance is used in personnel protection for the military (Sing e*t al.*,1985).

2.1.4: Properties of activated carbon

A gram of activated carbon can have a surface area in excess of 500 m^2, with 1500 m^2 being readily achievable Carbon aerogels, while more expensive, have even higher surface areas, and are used in special applications(jhadhav., 1991). Under an electron microscope, the high surface-area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behavior are usually done with nitrogen gas at 77 K under high vacuum, but in everyday terms activated carbon is perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of an atmosphere(Michael *et al.*,2004).

James Dewar, the scientist after whom the Dewar (vacuum flask) is named, spent much time studying activated carbon and published a paper regarding its absorption capacity with regard to gases In this paper, he discovered that cooling the carbon to liquid nitrogen temperatures allowed it to absorb significant quantities of numerous air gases, among others, that could then be recollected by simply allowing the carbon to warm again and that coconut based carbon was superior for the effect. He uses oxygen as an example, wherein the activated carbon would typically absorb the atmospheric concentration (21%) under standard conditions, but release over 80% oxygen if the carbon was first cooled to low temperatures(Michael *et al.*,2004).

Physically, activated carbon binds materials by van der Waals force or London dispersion force. Activated carbon does not bind well to certain chemicals, including alcohols, glycols, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does adsorb iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is used as an indication of total surface area (Michael *et al.*,2004).

2.1.5: Applications of activated carbon

Activated carbons (AC) 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.

Recently Activated Carbon filters have gained popularity among recreational users of Cannabis, and other smoking herbs for their use in effectively filtering out "Tar" from the smoke. They are becoming quick competition for vaporizers as they are only a fraction of the cost and achieve nearly the same thing.One major industrial application involves use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level (Smisek*et al.*, 1970).

Activated carbon, in 50% w/w combination with celite, is used as stationary phase in lowpressure chromatographic separation of carbohydrates (mono-, di and trisacchardes) using ethanol solutions (5–50%) as mobile phase in analytical or preparative protocols.In environment field activated carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as spill cleanup, Groundwater remediation , Drinking water filtration , Air purification , Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes(Smisek*et al*., 1970).

In medical applications activated carbon is used to treat poisonings and overdoses following oral ingestion. It is thought to bind to poison and prevent its absorption by the gastrointestinal tract. In cases of suspected poisoning, medical personnel administer activated charcoal on the scene or at a hospital's emergency department. Dosing is usually empirical at 1 gram/kg of body mass (for adolescents or adults, give 50–100 g), usually given only once, but depending on the drug taken, it may be given more than once. In rare situations activated charcoal is used in Intensive Care to filter out harmful drugs from the blood stream of poisoned patients. Activated charcoal has become the treatment of choice for many poisonings, and other decontamination methods such as ipecac-induced emesis or stomach pumping are now used rarely (Smisek*et al*., 1970).

2.1.6: Uses of activated carbon in produced water treatment

Activated carbon is extensively used in wastewater treatment. It is mainly used in tertiary treatment as a physico-chemical agent. Granular activated carbon is used in the form of a filtration bed. Waste water flows through this bed and organic molecules are adsorbed on the carbon surface. When the carbon becomes loaded with the adsorbed molecules and loses its adsorptive ability, it can be removed from the system and regenerated. Most commonly used commercial carbon for this process is made from bituminous coal (Faust and Aly, 1998).The advantages of using granul aractivated carbon for physico-chemical treatment are:

(1) Reduced land are are quirement (lessthanhalf) when compared to biological treatment plants,

(2) Higher levels of waste water treatment efficiency as compared to conventional biological processes

(3) reduced sensitivity to daily flow variations,

(4) Greater design flexibility,

(5) Greater operational flexibility and control (Hooper *et al*,1996).

Certain organic compounds in wastewater are resistant to biological degradation and contribute for the bad odor, taste, or color of the water. Even at low concentration, they are not readily removed by conventional treatment methods. Activated carbon has an affinity for organics and its use for organic contaminants removal from waste water is wide spread. The effectiveness of activated carbon for the removal of organic compounds from waste water by adsorption is enhanced by its large surface area, a critical factor in the adsorption process. The adsorption rate is influenced by carbon particle size, but not the adsorptive capacity, which is related to the total surface area.

Granular activated carbon is also used for providing tertiary treatment following conventional biological treatment. In this case, the carbon exhaustion rate usually ranges from 0.01–0.06g/l(0.1–0.5lb/1000gal). Contact time ranges from 15–30 min. A sin the case of secondary treatment, the granular carbon can be used for filtration as well as adsorption, or pre-filters can be provided. Granular activated carbon has been used to remove organics from a wide range of industrial waste water including dyes, phenolics, benzene, and chlorinated hydrocarbons. Many of these organics are toxic and not amenable to alternative biological process. The carbon exhaustion rate for industrial application can range from as low as 50 kg/ day (110 lb/ day) to greater than 50,000 kg/ day (110,000 lb/ day) depending on the type and concentration of contaminant, effluent objective, adsorbent configuration, and contact time. Contact times will generally range from30 –100 min (Hassler, 1963).

2.2: Petroleum coke

Petroleum Coke is a dark solid composed mainly of carbon, produced by the thermal decomposition and polymerization of heavy liquid hydrocarbon derived from crude oil (Franz, 2000). The coke produced from distillation residues tends to form the sponge coke, while coke produced from a cracking residue from the premium coke. The sponge type, due to its practically amorphous structure, has little commercial value, and may be an economical and environmental problem (Manoel*et al.*,2006).

2.2.1: History of petroleum coke

Petroleum coke was first made in the 1860s in the early oil refineries in Pennsylvania which boiled oil in small, iron distillation stills to recover kerosene, a much needed lamp oil. The stills were heated by wood or coal fires built underneath them, which over-heated and coked the oil near the bottom. After the distillation was completed, the still was allowed to cool and workmen could then dig out the coke and tar. In 1913, William Merriam Burton, working as a chemist for the Standard Oil of Indiana refinery at Whiting, Indiana, was granted a patentfor the Burton thermal cracking process that he had developed. He was later to become the president of Standard Oil of Indiana before he retired (Franz .,2000).

In 1929, based on the Burton thermal cracking process, Standard Oil of Indiana built the first delayed coker. It required very arduous manual decoking. In the late 1930s, Shell oil developed hydraulic decoking using high-pressure water at their refinery in Wood River, Illinois. That made it possible, by having two coke drums, for delayed decoking to become a semi-continuous process (Paul and Christopher.,1998).From 1955 onwards, the growth in the use of delayed coking increased. As of 2002, there were 130 petroleum refineries worldwide producing 172,000 tons per day of petroleum coke. Included in those worldwide data, about 59 coking units were operating in the United States and producing 114,000 tons per day of coke (Tulsa O., 2002*)*.

2.2.2.: Uses of petroleum coke

The coke product from a delayed Coker has many commercial uses and applications.The largest use is as a fuel (Paul and Christopher., 1998).

2.2.2.1: The uses for green coke are

- As fuel for space heaters, large industrial steam generators, fluidized bed combustions, Integrated Gasification Combined Cycle (IGCC) units and cementkilns
- In silicon carbidefoundries
- For producing blast furnace coke

2.2.2.2: The uses for calcined coke are

- As anodes in the production of aluminum
- In the production of titanium dioxide
- As a carbon raiser in cast iron and steel making
- Producing graphiteelectrodes and other graphite products such as graphite brushes used in electrical equipment
- In carbon structural materials

2.2. 3: Delayed petroleum coke based activated carbon

Delayed petroleum coke is produced in a coking drum heated to 480 C. volatile material is removed and the remaining by-product is broken up hydraulically and then removed from the drum. The delayed coker particles are irregularly shaped and display no visible porosity down to 500 microns. Particles range in size from a few microns to a few tens of millimeters (Jack *et al*, 1979).

The coke has an amorphous (non-crystalline) structure, where 92% of the carbon atoms are aromatic (Majid *et al*, 1989). The reactivity of delayed petroleum coke, in terms of oxidation, is extremely low (Watkinson *et al*, 1989). The proximate analysis, ultimate analysis and heating value of this coke are given in Table 2.1.

Table 2.1: Properties of delayed petroleum coke(Watkinson *et al.*, 1989)

Parameter	Proximate Analysis W %
Ash	3.0
Volatile	11.9
Moisture	1.8
Fixe carbon	83.3

Table 2.2:Coke ash content in w/w% (Majid *et al.*, 1989)

Parameter	content in w/w%
SiO_2	41.7
Al_2O_3	19.2
Fe	16
Ti	1.5
Ni	1.6
V	2.8

Coke consists of solid, spherical particles ranging, insize; from a few microns to 20 mm. Spherical particles have an "onion skin" internal structure consisting of 30 to 100 layers of coke (Panfilo, 1995). The high temperature conditions produce non-porous graphitized carbon as indicated by its low leaching (Jack *et al.*, 1979). All the carbons are aromatic and about 45 % of the carbons are bonded to hydrogen atoms (Majid *et al.*, 1989).

The activation of petroleum coke has been investigated since the 1980s by various investigators, who obtained specific surface areas in the rangeof 80 m^2 g^{-1} to 3000 m^2 g^{-1}, depending on experimental conditions. The porosity of the resulting activated coke is influenced by the impregnation ratio (KOH/coke) and activation temperature, but there is no agreement regarding which variable is the most significant and how these variables affect the activated petroleum coke porosity (Manoel, 2006).

A series of activating agents have been reported for the chemical activation process, including phosphoric acid, zinc chloride, and alkaline metal compounds.KOH as one of the typical alkaline metal compounds is widely used for the chemical activation of coal precursor, chars and petroleum coke. It has been reported that the chemical reactions between hydroxides (KOH or NaOH) and carbon occurred during the activation process and it played an important role in the development of the porosity of the activated carbon. Yamashita and Ouchi studied the interactions of alkaline hydroxides with carbonaceous material and proposed an activation process as follows:

$$4KOH + {=}CH_2 \longrightarrow K_2CO_3 + K_2O + 3H_2 \qquad (1)$$

$$K_2O + C \longrightarrow 2K + CO \qquad (2)$$

$$K_2CO_3 + 2C \longrightarrow 2K + 3CO \qquad (3)$$

Clearly, =CH2 species is necessarily required to react with KOH to produce K2CO3 and K2O. The alkyl species on the surface of the precursor played a key role in the chemical activation (Yamashita *et al.*,1982).

The effect of different amount of KOH and NaOH on the development of carbon porosity with coal as carbon precursor reported by Ehrburger The formation of K_2CO_3 on the carbons impregnated with KOH was observed with a simultaneous evolution of CO_2 and CO. A C–O–K species formed at the carbon surface was proposed to act as active sites in the gasification process (Ehrburger*et al.*,1986).Not only _active sites_ but also micrographite crystallites may have great effect on the chemical activation process. Activated carbons are not composed of well crystalline graphite, but disorderly micrographite crystallites (Kaneko and Ishii., 1982).

Porous carbons with surface area around 2500–3000 m^2/g have been produced from the MPC coke byco-activation with KOH and

H_2O as active agent. Theco-activation process with KOH and H_2O as active agent,which has been rarely reported as active agent to prepareporous carbons in the same procedure, is the easiest methodfor making porous carbons with high surface areas. The weight ratio of KOH to petroleum coke is 2–1, which is much shorter than the optimum ratio reportedthat is normally more than 3–1. The optimumactivation time for preparing high surface area porouscarbons from MPC in the co-activation method with KOH-H_2O as active agent is about 25 min,which is much shorter than the optimum time reported that is normally around 2 hrs(Mingbo*et al.*, 2004).Regarding the chemical activation of petroleum coke the proposed process was appropriate to produce activated carbons with a wide range of porous textures,.Furthermore, the process obtains activated carbons with high surface areas (up to 2500 $m^{2\cdot}g^{-1}$) and high pore volume (up to 1,5 $cm^3.g^{-1}$) (Méndez*et al.*,2005).

. Besides different activation methods, the process parameters in a certain activation method, such as the activation time in the co-activation method, also have effect on the pore structure of the porous carbons. Increasing the activation time unto 25min in the co-activation method increased the BET surface area of porous carbons made from MPC coke. The yield of porous carbon in KOH+H_2O activation in this work is much less than that of KOH activation (Mingbo*et al.*, 2002).

2.3: Produced water characteristics

The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water properties and volume can even vary throughout the lifetime of a reservoir. If water-flooding operations are conducted, these properties and volumes may vary even more dramatically as additional water is injected (Breit e*t a*l. 1998).

2.3.1: Major components of produced water

Knowledge of the constituents of specific produced waters is required for regulatory compliance and for selecting management/disposal options such as secondary recovery and disposal. Oil and grease are main constituents of produced water that receive the most attention in operations, while salt content (expressed as salinity, conductivity, or TDS) is a primary constituent of concern in onshore operations. In addition, produced water contains many organic and inorganic compounds. These vary, greatly, from location to another and even in the same well.

2.3.2: Produced water from oil production

Organic and inorganic components of produced water discharged fromoffshore wells can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates (Tibbetts*et al*, 1992).

In addition to its natural components, produced waters fromoil production may also contain groundwater or seawater (generally called “source” water) injected to maintain reservoir pressure, as well as miscellaneous solids and bacteria. Most produced waters are more saline than seawater (Cline, 1998). They may also include chemical additives used in drilling and producing operations and in the oil/water separation process. Treatments chemical are typically complex mixtures of various molecular compounds. These mixtures include:

- Corrosion inhibitors and oxygen scavengers to reduce equipment corrosion.
- Scale inhibitors to limit mineral scale deposits.
- Biocides to mitigate bacterial fouling.
- Emulsion breakers and clarifiers to break water-in-oil emulsions and reverse breakers to break oil-in-water emulsions.
- Coagulants, flocculants, and clarifiers to remove solids.
- Solvents to reduce paraffin deposits (Cline, 1998).

In produced water, these chemicals can affect oil/water partition coefficient, toxicity, bioavailability, and biodegradability (Brendehaug*et al.,* 1992). With increased development of subsea oil fields, many of these additives will be required, to assure flow in subsea pipelines (Georgie *et al*., 2001).

2.3.3 Produced water treatment

Both formation and injection water are produced alongside oil and, as oil fields age, the amount of produced water increases. Large quantities of contaminated water have a negative, environmental, impact if not handled properly. No single piece of equipment can tackle the complex process of treating produced water to meet increasingly stringent regulations for discharge or re-use (John *et al*, 2004).

2.3.3.1: Primary produced water treatment

The primary treatment of produced water in itself involves multiple techniques from upstream sand removal utilizing solid/liquid hydrocyclones at wellhead conditions through multi-phase separators and collection vessels to further solid/liquid and liquid/liquid hydrocyclones. Two phase (gas/liquid) and three phase (gas/oil/water) separators (also known as free water knockout separators) to international standards. The liquids (oil and water) leave through different valves at the bottom of the vessel. Gas leaves from the top of the vessel.

2.3.3.2: Secondary produced water treatment

After primary treatment of produced water gives the first oil cut, the secondary treatment conditions produced water and solids in preparation for discharge or further polishing. Hydrocyclones provide excellent removal of sand and free oils in water but the latest, stringent regulations often require complementary technologies to reduce the levels of oil and other contaminants. Secondary treatment of produced water has to tackle the issue of dissolved hydrocarbons in the water.

2.3.3.3: Tertiary produced water treatment

As the oil content in water decreases, it becomes more difficult to remove oil contamination further. Primary and secondary water treatment systems meet 90% of requirements for discharge limits. However, further water polishing is required, this can be achieved using tertiary produced water treatment through additional filtration – a final cleaning stage before water is discharged overboard requires a range of products including nutshell media filters, coalescing filters and adsorption filters (John *et al*,2004).

2.4: Adsorption principles

Planar surface of the micropores contributes mostly to the surface area, which is responsible for the adsorptive property of the activated carbon. The adsorption on these surfaces is mostly physical due to weak Van der Waals forces. During the process of carbonization, a large number of unpaired electrons, which are resonance stabilized, are trapped in the microcrystalline structure.

2.4.1: Factors affecting adsorption

2.4.1.1: Surface Area, pore structure, and pore size distribution:

Surface area is one of the principle characteristics affecting the adsorptive capacity of an adsorbent, since the adsorption process results in a concentration of solutes at the surface. Pore structure and chemistry of activated carbon are strongly dependent on pyrolysis temperature, composition, and structure of the raw materials (Girgis*et al*,1994). Most of the macropores are formed during the pyrolysis process in the void volume filled by the binder. The shaping process of the granules determines the macropore system. Granule size depends on the forming pressure, particle size and particle size distribution of the starting material in the granule. Since surface properties of the GAC are a function of the precursor, pyrolysis and activation conditions, it is essential to characterize them with respect to the number and type of the chemical group on the surface, the polarity of the surface, pore size distribution and total surface area. (Ahmedna*et al*., 2000).

2.4.1.2: Particle Size

Activated carbon is a complex network of pores of varied shapes and sizes. The shape includes cylinders, rectangular cross sections, as well as many irregular shapes and constrictions. The size can range from less than 10 Å to over100,000 Å. Pore size distributions; will depend on the source materials used and on the method and extent of activation. Pores are often classified as macropores, mesopores, and micropores (Hassler, 1963).

2.4.1.3: Chemistry of the surface

There are two methods of adsorption, namely, physisorption and chemisorption. Both methods take place when the molecules in the liquid phase becomes attached to a surface of the solid as a result of the attractive forces at the solid surface (adsorbent), overcoming the kinetic energy of the contaminant (adsorbate) molecules.

Physisorption occurs, as a result of energy differences and/or electrical attractive forces (weak Van der Waals forces), the adsorbate molecules become physically fastened to the adsorbent molecules. This type of adsorption is multi-layered; that is, each molecular layer forms on the top of the previous layer with the number of layers being proportional to the contaminant concentration. More molecular layers form with higher concentrations of contaminants in solution.

When a chemical bond is produced by the reaction between the adsorbed molecule and the adsorbent, chemisorptions has occurred. Unlike physisorption, this process is one molecule thick and irreversible, because energy is required to form the new chemical compounds at the surface of the adsorbent, and energy would be necessary to reverse the process. The reversibility of physisorption is dependent on the strength of attractive forces between adsorbate and adsorbent. If these forces are weak, desorptionis readily affected.

2.4.2: Nature of the adsorbate

2.4.2.1: Effect of pH

The adsorption of non-electrolytes by activated carbon from aqueous systems is generally not affected by the solution pH, although some exceptions can occur. However, the effect of pH on the adsorption of weak electrolytes, both acids and bases, is quite pronounced. Both undissociated and ionized form of a species can be adsorbed on activated carbon, with undissociated form being more strongly adsorbed than ionized forms (Faust and Aly, 1998).

2.4.2.2: Effect of inorganic ions

The inorganic composition (Ca^{2+}, Mg^{2+}, etc) of water can also have an important effect on adsorption of selected organics from water by activated carbon. Calcium ion complexes Ca^{+2} adsorption. Many other divalent cations can act in similar manner, but Ca^{+2} has special interest because of its ubiquitous distribution in natural water. Other inorganic ions include Cu^{2+},Zn^{2+},Ag^{2+}, and Pb^{2+} commonly found as contaminants in wastewater.

2.4.2.3: Effects of temperature

Since the process of adsorption is spontaneous, it is accompanied by a decrease in the system's free energy. There is always a decrease in entropy due to loss of degree of freedom of the solute in passing from the dissolved state to the adsorbed state. The decrease in entropy drives a decrease in enthalpy (ΔH)where the two are related by.

$$\Delta H=\Delta G+T\Delta S$$

The enthalpy change (ΔH), for physical adsorption is in the range of 2-15 kcal/mol. An increase in temperature therefore results in a reduction of the equilibrium adsorptive capacity.

2.4.3: Adsorption equilibria

Adsorption from aqueous solutions involves concentration of the solute on the surface. As the adsorption process proceeds, the sorbed solute tends to desorb into the solution. Equal amounts of solute eventually are being adsorbed and desorbed simultaneously. Consequently, the rates of adsorption an desorption will attain an equilibrium state. The position of equilibrium is characteristic of the solute, adsorbent, solvent, temperature, and pH. Several models are used for the description of the adsorption data of which the Langmuir and Freundlich models are the ones most commonly used.

Several researchers have shown the impact of influent pH on the adsorption , Relationship between the relative adsorption capacity and pH for different source waters and a bituminous-coal-based GAC (Hooper, Summers, and Hong, 1996). A decrease in the pH of one unit yielded a 6 percent increase in adsorption capacity in their study.

2.4.3.1: Langmuir adsorption isotherm

Langmuir’s model is characterized by the following conditions:

1) The molecules are adsorbed on definite sites on the surface of the adsorbent

2) each site can accommodate only one molecule (monolayer);

3)The area of each site is a fixed quantity determined solely by the geometry of the surface; and

4) The adsorption energy is the same at all sites.

In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir adsorption isotherm is expressed as:

$$X = \frac{\mathrm{X_m\ b\ C_e}}{1 + \mathrm{bC_e}}$$

Where;

X = x/m, the amount of solute adsorbed x per unit weight of adsorbent m

C_e= equilibrium concentration of the solute

X_m= amount of solute adsorbed per unit weight of adsorbent required for Mono layer capacity

b = a constant related to the heat of adsorption

This equation can be written in the form:

$$C_e = \frac{1}{bX_m} + \frac{C_e}{X_m}$$

When C_e/ X is plotted vs. C_e a straight line, should result, having a slope $1/X_m$ and an intercept 1/b X_m. The monolayer capacity Xm determined from the Langmuir isotherms defines the total capacity of the adsorbent (Kanô*et al*, 2000).

2.4.3.2: Freundlich adsorption isotherm

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as:

$$\frac{x}{m} = kC_e^{1/n}$$

Where,

x = the amount of solute adsorbed.

m = the weight of adsorbent.

C_e= the solute equilibrium concentration.

k, 1/n = constants characteristic of the system.

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C_e$$

Plotting log x/m vs. log C_e, a straight line is obtained with slope of 1/n, and log k is the intercept of log x/m at log $C_e = 0$ ($C_e = 0$). The value of 1/n obtained for adsorption of most organic compounds by activated carbon is < 1. The Freundlich equation indicates the adsorptive capacity or loading factor on the carbon, x/m, is a function of equilibrium concentration of the solute. Therefore higher capacities are obtained at higher equilibrium concentrations (Kanô*et al*, 2000).

2.5: Removal of organic pollutants

The ability of granular activated carbon to remove abroad spectrum of organic compounds from water is well documented (Toles *et al.* ,1997; Johns, *et al.*,1998; Rockstraw,2001; Wartelle, *et al.*,2001**.** In recent decades the quality of many water supplies has been adversely affected by factors associated with the tremendous growth in the production of industrial chemicals many of the contaminants are highly stabilized organic compounds that are not destroyed by biological or chemical treatment of wastes, and they often survive the self- purification that normally occurs in moving streams. The organic contaminants are not appreciably removed by the steps of coagulation, chlorination, and filtration employed in water purification plants. Activated carbon is used in sufficient quantities to make the water palatable and eliminate foaming, and only the more odorous ingredients will give a perceptible taste at the dilutions usually present (Rockstraw, 2001).

Some organic contaminants are more adsorbable than others. Organic solvents such as trichloethylene and aromatic solvents such as toluene are adsorbable due to their low solubility in water. Higher molecular weight compounds, such as polynuclear aromatics, and surfactants, are also effectively adsorbed. Conversely, water-soluble compounds such as alcohols and aldehydes are poorly adsorbed (StenzelL., 1993). Volatile organic compounds (VOC) such as low molecular weight chlorinated solvents and aromatics are generally treated with air stripping or granular activate dcarbon. Air stripping yields 95-99% removal of VOCs. However due to environmental issues, discharge of VOCs into the atmosphere limits its utility. Granular activated carbonon the other hand can remove both volatile as well as non-volatile compounds with effective reduction of organic contaminants to undetectable limits and prevent their discharge back in atmosphere (Stenzel L, 1995).

2.6: Removal of inorganic pollutants

Toxic metal compounds not only contaminate surface water sources (seas, lakes, ponds and reservoirs), but also contaminate underground water intrace amounts by leaching from the soil after rain and snow. Toxicity of heavy metals has triggered a number of studies aimed at removal of the metal ions from aqueous solutions. In treatment of waste water streams containing heavy metals, precipitation is a commonly used treatment approach. However, the effectiveness of precipitation depends strongly on the composition of the waste water. In addition, precipitation produces sludge that requires further treatment. Ion exchange and adsorption have been alternative methods for removing metals. In the past, most studies focused on the adsorption equilibrium of single-species metal ions, while less result appeared in the literature on multi-species metal adsorption. In addition, a survey of the relevant literature on adsorption of heavy metals onto activated carbon shows that the adsorption kinetics and its modeling simulation have not been thoroughly studied (Hassler., 1963).

CHAPTER THREE

3.1: Materials

3.1.1: Samples

Three Petroleum coke samples, 1000 g, from Delayed Coker of Khartoum Refinery Company were randomly collected in a polyethylene bags and carried to the laboratory. 1.0 L of produced water sample was also collected from the inlet valve of produced water bond at Baleela oilfield-Sudan.

3.1.2: Chemicals

All chemicals used are of Analyticalgrade except where stated.

3.2: Methods:

3.2.1: Preparation of activated carbon:

The chemical activation experiments were carried out impregnating 1.0 g of petroleum coke with an aqueous solution of potassium hydroxide (KOH) according to the impregnation ratio. The resultant mixture was evaporated at 150 **C**, heated up by a electric furnace (Labtech- LEF TYPE P, Daihan-India) with heating rate control 25**C**/ min and temperature control with different activation times starting from 30, 45 and 60 min and impregnation ratios were 1:1 to 1:5, activated carbon produced were washed with 500 ml hydrochloric acid 10% (Density 1.18 g/ml,conc. 37% ,Scotte Science – UK), washed with hot and cold distilled water to remove the alkali metal and ashes until the filterate neutral, Table 3.1.

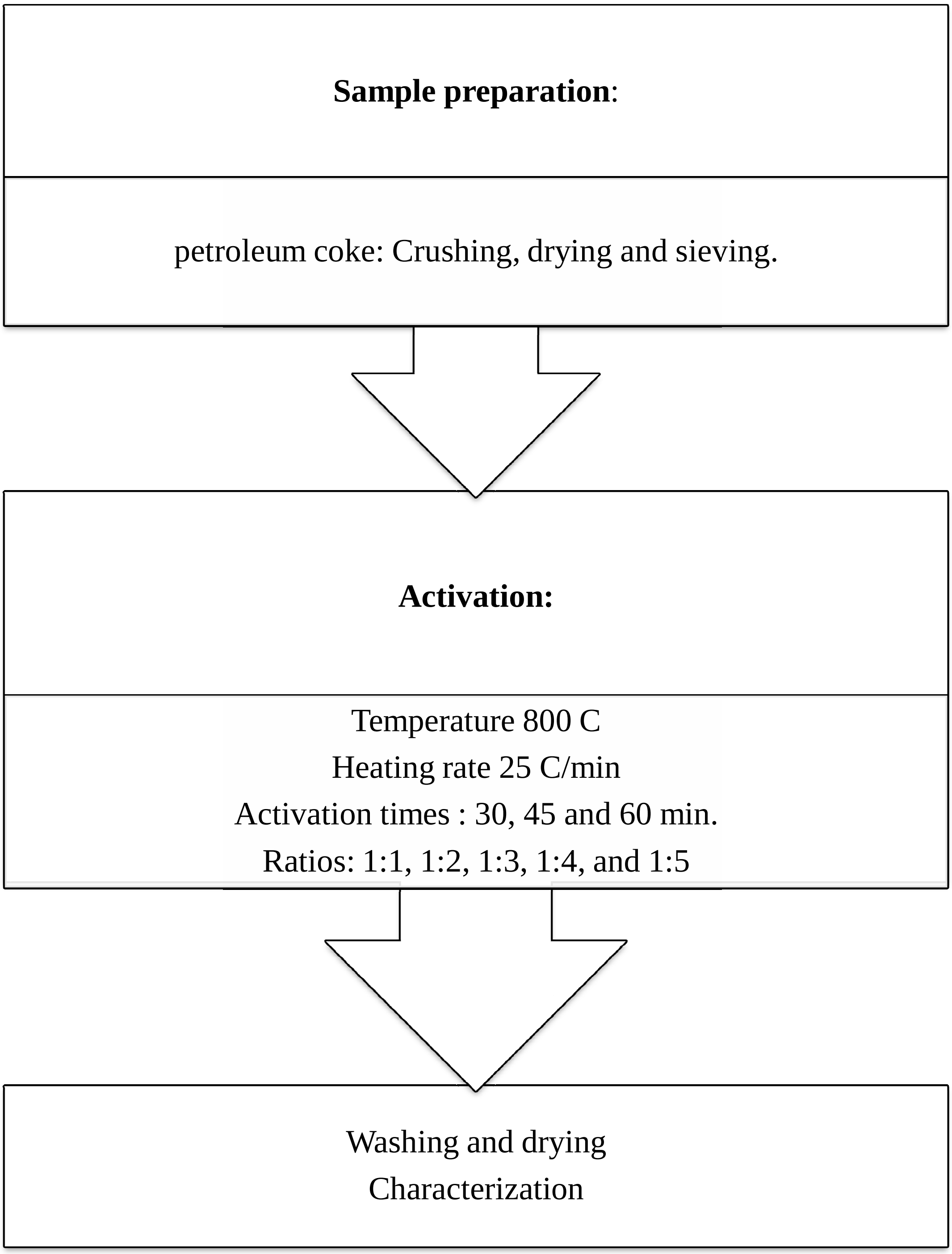

Fig.3.1: Flow diagram of activation process.

Table 3.1: parameters and conditions used in the activation experiments:

Ratio in g (Coke:KOH)	Activation temp./C˚	Activation time/minute
1:1	800	30
1:1	800	45
1:1	800	60
1:2	800	30
1:2	800	45
1:2	800	60
1:3	800	30
1:3	800	45
1:3	800	60
1:4	800	60
1:5	800	60

3.2.2: Activated carbon characterization

3.2.2.1: Preparation of Coke and AC samples with AAS

5.0 g of raw petroleum coke and activated carbon were accurately weighted using a electric sensitive balance, the solution of Tri-acid was prepared by adding HNO_3 10 %, H_2SO_4 1% and $HClO_4$ 4%, 15 mLs of these solutions were added to each sample and were cooled to room temperature, filtered through a filter paper and diluted to 100 mLs, heated in a hot plate at 200 **C** for 3 hrs, diluted to 100 mLs.

3.2.2.2: Preparation of calibration curves of heavy metals by AAS:

Hallow cathode lambsfor each element wereselected, series of standard solutions of Zinc (0.5,1.0 and 1.5 ppm) ,nickel (2.0,4.0 and 6.0 ppm) and chrome (3.0,6.0 and 9.0 ppm) were prepared using standard solution stock of 1000 ppm, then, using AAS (Thermo Scientific-ICE 3000, USA), absorbance of each solution was measured at specific wavelength according to standard analytical method using SOLAAR softeware.

3.2.2.3: Fourier Transform Infrared Spectroscopy

FTIR analysis was performed using FTIR-84005 (SHIMADZU Corporation Kyoto, Japan). 0.1 g was mixed with 1 g of KBr, spectroscopy grade (Sharlau), in a mortar. Part of this mix was introduced in a cell connected to a piston. The mix was converted to a solid disc which was placed in an oven at 105 **C** for 4 hours to prevent any interference with any existing water vapor or carbon dioxide molecules, transferred to the FTIR analyzer and a corresponding spectrum was obtained showing the wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library.

3.2.2.4: Iodine Number (IN)

2 drops of Starch solution were added to 10 mLs of 0.1N Iodine solution, the pale yellow color of Iodine Solution turned blue, the solution was titrated against 0.05 N sodium thiosulphate until it became Colorless (B) , 0.2 g of Activated carbon were added to 40 mLs of 0.1N Iodine solution, the flask was shaken for 4 minutes and then filtered, the filtrate was collected in a dry flask and 10 mLs of the filtrate were titrated against

standard sodium thiosulphate solution using starch as indicator (A), normality of Iodine filterate was calculated.

Molarity of sodium shiosulphate was calculated from the following equation.

Calculations involved in iodine value estimation:

Iodine value: C x Conversion factor; mg/g.

Factor: Mol wt. of iodine (127) x normality of iodine x 40 / Wt. of carbon x B.

C=B-A.

(European Concil of chemical manufacturers, ferderations ,test methods of activated carbon., 1986).

3.2.2.5: Methylene blue (MB):

5.0 g of MB was dried at 110**C** for 2 hours before use. All of the MB solutions were prepared with distilled water,stock solution of 1000mg/L was prepared by dissolving 1.0 g of MB in 1000mLs distilled water (Omomnhenle *et al*., 2006), experimental solution was prepared by diluting the stock solution with distilled water , 10 and 50mg/L. The concentration of MB was determined at 660nm by the UV–visible spectrophotometer (Livo Pond- Tintometer, GmbH, Germany) (Chongrak *et al*., 1998), a calibration curve of optical densities against methylene blue concentrations was obtained by using standard MB solutions of known concentrations at pH values between 3 and 4. A quantity of 0.1 g of AC was added to 100 ml of 57 mgL-1, the flask was shaken for 4 minutes and then kept for 24 hrs., the filtrate was collected in a dry flask and 10 ml of the filtrate absorbance were measured.

MB is calculated by the equation:

$$Q_{eq}\,(mgg^{-1}) = \frac{(C_0 - C_e\,)X\,V}{M}$$

Where: C_0 (mg /L$^{)}$= concentration of the MB solution at starting time (t = 0).

C_e (mg/L) = concentration of the MB solution at equilibrium time.

V (L) = volume of the solution treated and

M (g) is the mass of the adsorbent. (European Concil of chemical manufacturers, ferderations ,test methods of activated carbon., 1986).

3.2.3: Application of activated carbon

3.2.3.1: Determination of organic constituents:

Calibration curve was constructed by using standard solution, dispersed oil absorbance was measured for each standard concentration using colorimetric method (LivoPond-Tintometer, GmbH, Germany at 420 nm) recommended by Standard Method for Examination of Water and Wastewater (Clesceri et. al., 1998) , n-hexane was the extraction solvent , zeroed and then the absorbance of each standard concentration was read and plotted against the logarithm of the concentration using Microsofte office 2007 excel sheet.

Variation of dispersed of oil with equilibrium time at different pH

0.1 g of AC was added to 50 mLs of produced water samples, the pH of each sample was adjusted to 2,4,6,8 and 10 using 5 M Hydrochloric acid and 5 M Amonium solution , calibrated pH-meter (PH-METER- HI9025, HANNA –UK) was used to measure the pH of samples. Initial concentration of each sample was measured and recorded, after 24, 48 and 72 hrs, 1 ml of the water was taken and dissolved oil absorbance was read and calculated. .

Determination of dispersed oil adsorption capacity

Initial concentration of dissolved oil in produced water sample was measured, a series of different weights of the activated carbon ranging from 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 g was accurately weighted using (Shimatzu -PW254, SN:AE438471) sensitive digital balance and added to 50 ml of produced water, the pH was adjusted to 4, after equilibrium, the concentration of each sample was measured and the logarithm of X/m was plotted against the logarithm of the residual concentration.

3.2.3.2: Determination of inorganic constituents:

Determination of Zinc (+2) adsorption capacity

Solution of 120 mg/L of Zinc (II) was prepared, 100mLs were mixed in 250 mLs beakers with 0.01, 0.03, 0,06,0.09 and 0.12 g, the mixtures were stirred for 15 min and allowed to settle for 48 hrs before they were filtered. The residual metal ion concentrations of the filtrates were determined using AAS (Thermo Scientific-ICE 3000, USA).

4: Results and discussion

4.1: Activated carbon characterization

4.1.1.: Activated carbon yields

Results show that the activated carbon (AC) yield mainly depends on the amount of activation agent added (KOH), Table 4.1 and fig. 4.1 show that the increasing of the activation agent amount increases the yield and that can be attributed to the excess amount of the activation agent loaded on the coke during impregnation which prevents volatilization of carbon during activation (Jin*et al*, 2012).

4.1.2: Determination of heavy metals

Table 4.2 shows the result of heavy metals; namely, Zinc, Nickel and Chromium , they were measured inbothraw coke and produced activated carbon (AC), to know their concentration limits, since they are considered as a harmful pollutant, therefore their presence in the activated carbon is not recommended.

4.1.3: FTIR analysis

The FT-IR spectroscopic study of the produced activated carbon (AC) is shown in Figure 4.2. The sample showed four major absorption bands at 2900-3500 cm^{-1}, 1300-1750 cm^{-1}, 1000-1250 cm^{-1} and 450-900 cm^{-1}. A wide band with two maximum peaks can be noticed at 2930 and 3450 cm^{-1}. The band at 3452 cm^{-1} is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water, while the band at 3037 cm^{-1} is attributed to C-H interaction with

Table 4.1: yield at various temperatures and ratios:

Coke:KOH	Yield % (30 min)	Yield % (45 min)	Yield % (60 min)
1:1	58.20	21.20	28.40
1:2	45.10	25.30	22.00
1:3	45.00	52.10	50.00
1:4	N/D	N/D	68.70
1:5	N/D	N/D	61.00

N/D= Not determined.

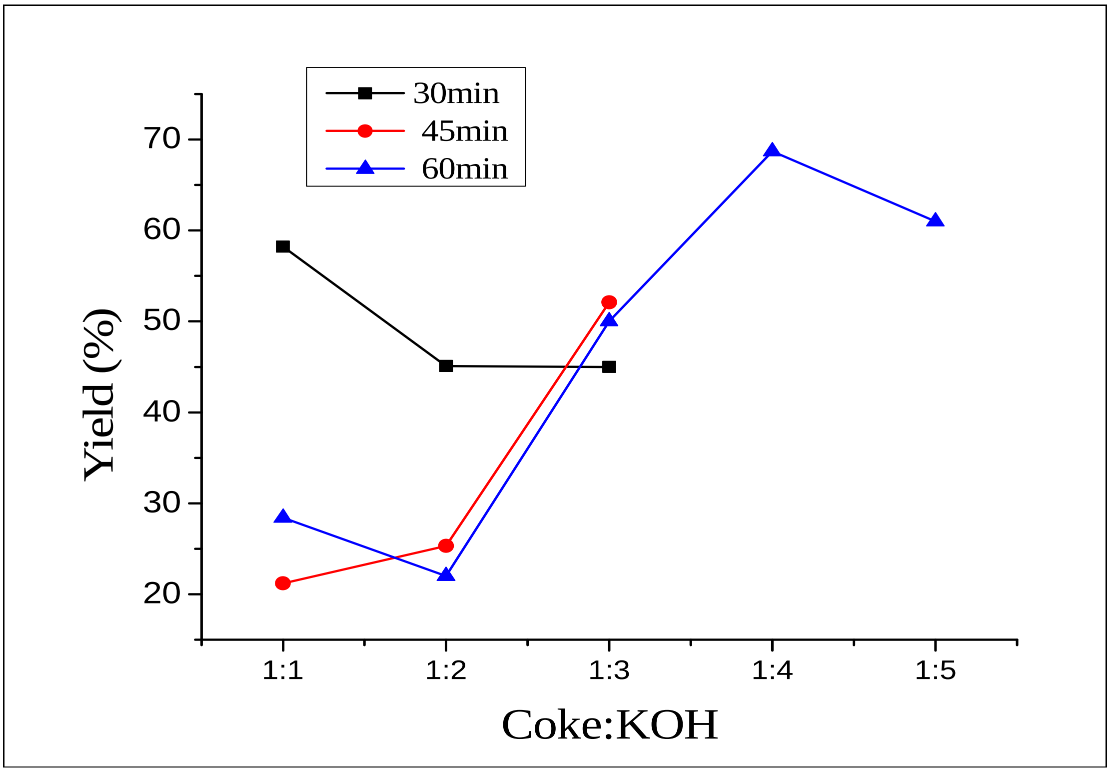

Fig. 4.1: Effect of activation time and different ratios AC yield.

Table 4.2: Heavy metals in petroleum coke and AC.

Heavy metal	**Petroleum coke/mgL^{-1}**	**AC/ mg L^{-1}**
Zinc	0.0668	0.0546
Nickel	1.8863	0.2089
Chrome	0.1400	0.9800

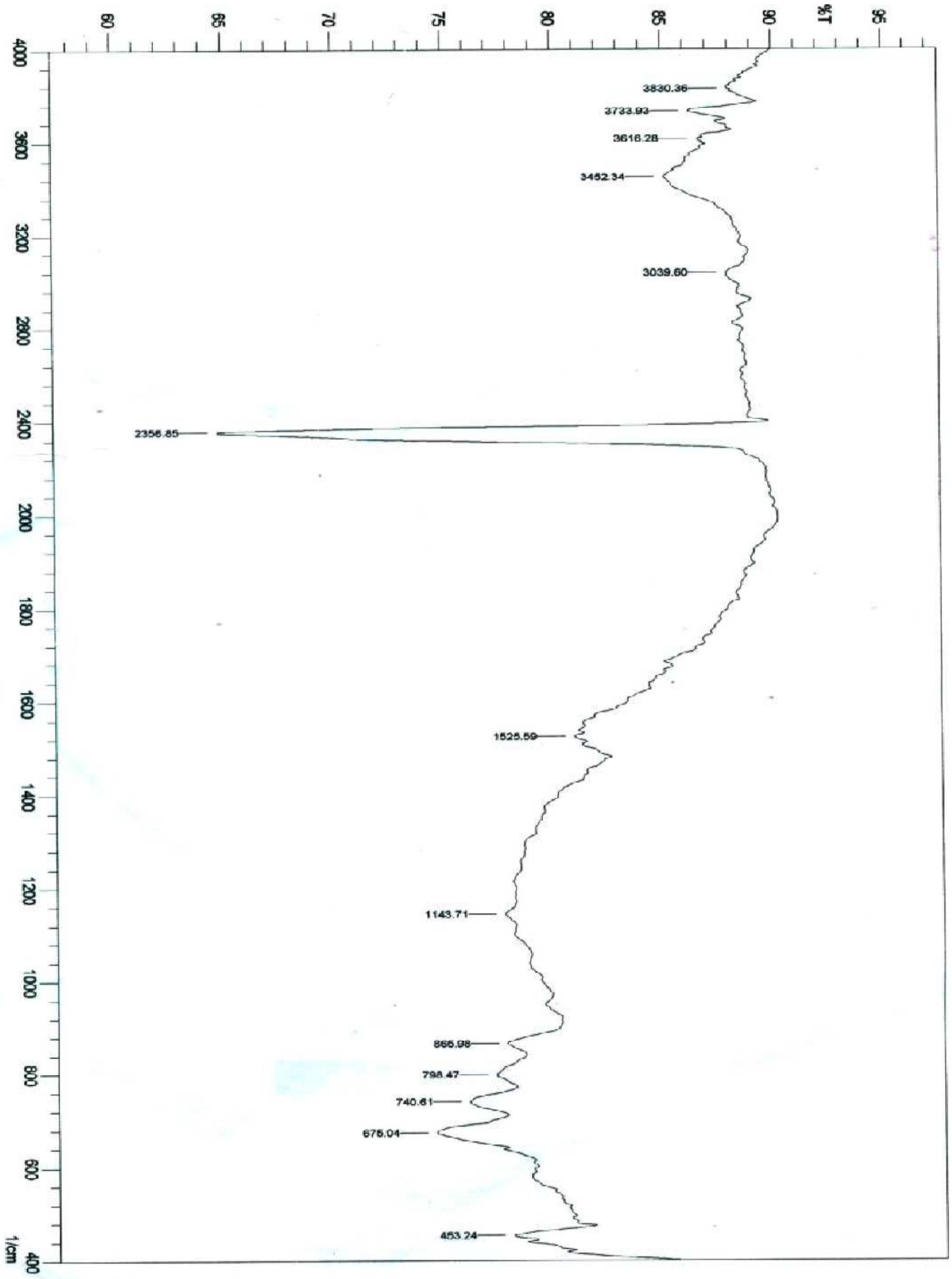

fig.4.2: FTIR spectra of activated carbon (AC)

The surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm^{-1} have also been attributed to the hydrogen-bonded OH group of alcohols and phenols(Yang and Lua ,2003; Puziy*et al*., 2003). In the region 1300-1750 cm^{-1}, amides can be distinguished on surface of the activated carbon (AC) which has two peaks at 1640 and 1450 cm^{-1}. The two peaks at 1143-1193 cm^{-1} yield the fingerprint of this carbon. The sharp absorption band at 1087 cm^{-1} is ascribed to either Si-O (Misra*et al*, 2005) or C-O stretching in alcohol, ether or hydroxyl groups. (Park *et al*,1997),(Attia*et al*,2006) The band at 1143 cm^{-1} can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C-ring)(Lapuente*et al*,1998), Si-O-Si stretching mode as a result of existing alumina and silica containing minerals (Calzaferri and Imhof, 1996).The region 450-750 cm^{-1} show two bands in the 480 and 485 cm^{-1} which are associated with the inplane and out-of-plane aromatic ring deformation vibrations (Socrates G., 1994). Peaks at 598 and 671 cm^{-1} are assigned to the out-of-plane C-H bending mode. These spectra were also suggested to be due to alkaline groups of cyclic ketons and their derivatives added during activation (Guo and Lua, 1999).

4. 1.4: The effect of Coke toKOH ratio on IN and MB

Figs. 4.3 and 4.4 show the increase in IN and MB values with increase of the ratio, probably, due to sufficient amount of KOH to react with the coke to efficiently create the internal pores and deterioration of micropores structure to form mesopores and macropores (Jin*et al*, 2012).This was investigated with iodine number and methylene blue test according to the global reaction (Yamashita and Ouchi, 1982).

4.1.5: The effect of activation time on IN and MB

As it can be observed in figs. 4.5 and 4.6, and with changing the activation time from 30 to 45, the IN and MB increased. The suggested reason is that more diffusion of active agent during activation (Mingbo*et al*., 2004). Moreover, It can be noticed that the suitable activation time is 60 min in terms of IN and MB and this is much shorter than the time reported in literature that is normally around 2 h (Ahmadpour*et al*, 2001).

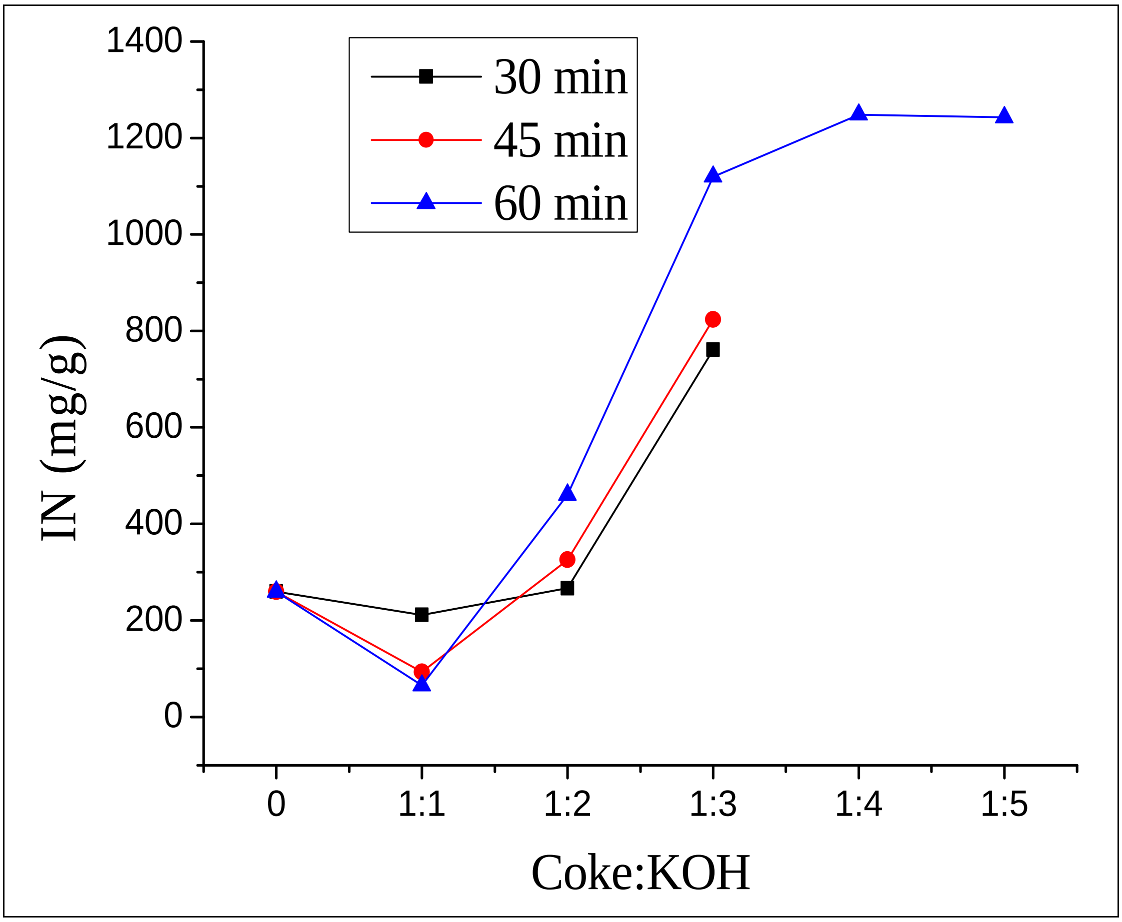

Fig. 4.3: The variation of Coke: KOH ratio with IN.

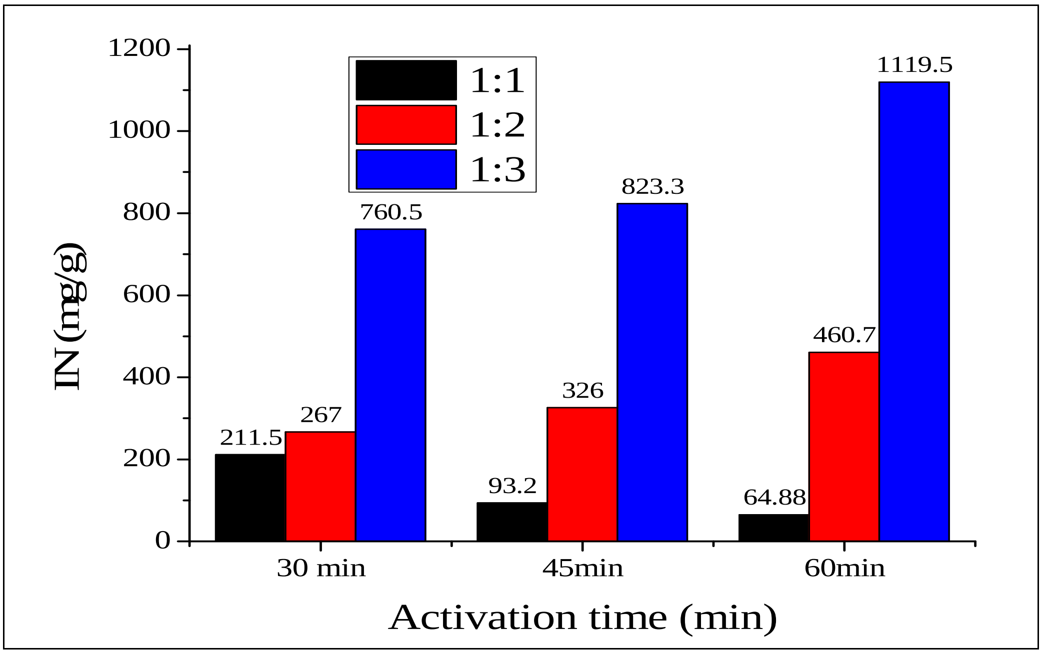

Fig. 4.4: The variation of Activation time with IN.

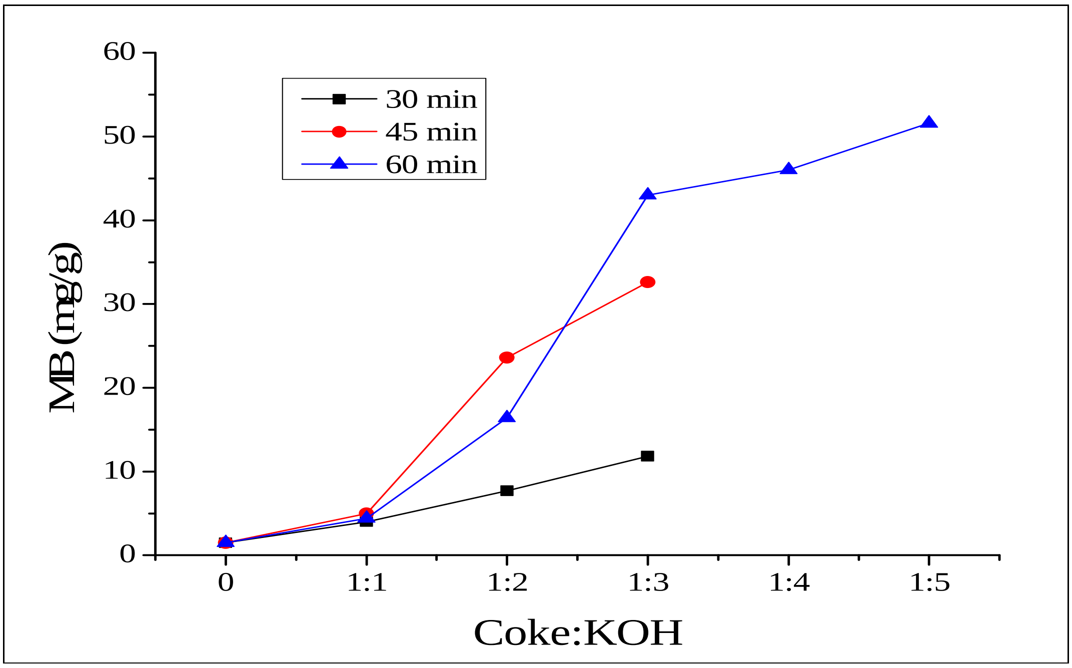

Fig. 4.5: The variation of Coke: KOH ratio with MB at 800 C.

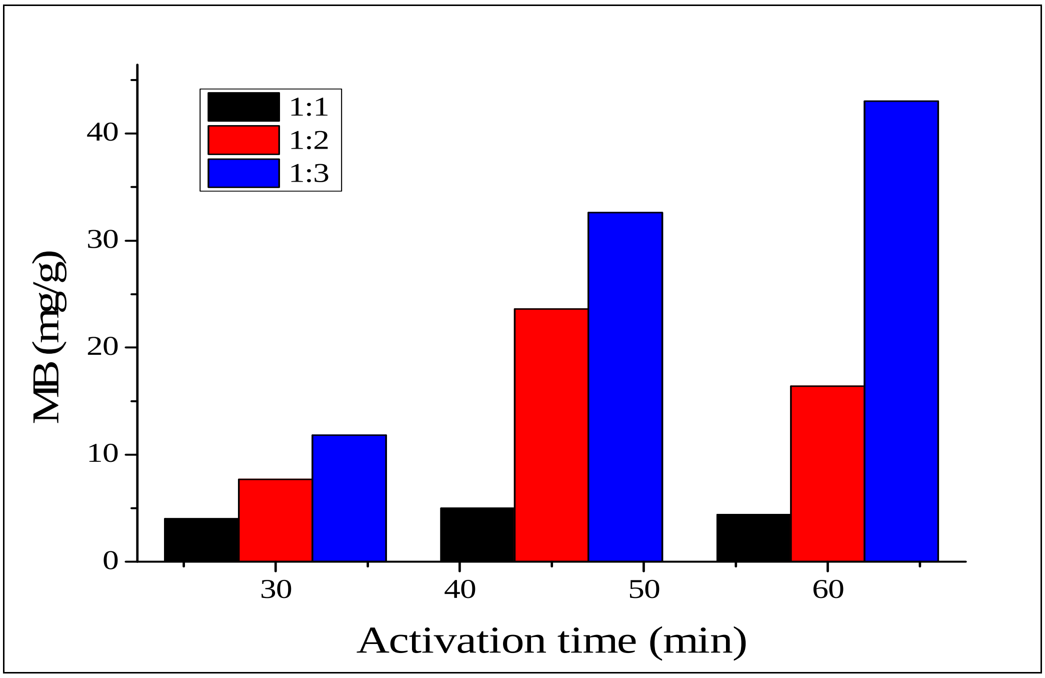

Fig. 4.6: The variation of Activation time with MB.

4.2: applications of activated carbon (AC)

4.2.1: Variation of dispersed oil adsorption with equilibrium time at different pH

Fig.4.7 presents the dispersed oil adsorption from produced water withpH ranging from 2.0 to 10.0. The initial dispersed oil concentration of the untreated produced water was 742 mg L^{-1}. The results showed that prepared activated carbon (AC) has higher adsorptive capacity at pH 4, and with the increasing in thesolution pHto 6, 8 and 10 the uptake of the dispersed oil decreased dramatically, this finding is consistent with the results obtained by other researchers (Anirudhan and Ramachandran, 2007) who observed that the uptake of humic acids by an organoclay decreased dramatically as the pH of the solution was increased from 3 to 10. The proposed explanation is that the organic compounds in produced water can be polar as well as nonpolar, thus, dispersive interactions between the aromatic rings and the π electrons of the graphene can play an important role and hydrogen bonding of organic compounds. Beside, electrostatic attractive between the charged surface and organic compound can play an important role (Anirudhan and Ramachandran, 2007). Adsorption equilibrium time was also investigated after different contact time starting with 24 hrs for each pH and it found that with increasing in the contact time the amount of dispersed oil adsorbed were also increased and reached the equilibrium after 72 hrs.

4.2.2: Adsorption capacity of dispersed oil

Data presented from table 4.3 in fig. 4.8 can be used to determine the required carbon dosage to the desirable treatment concentration. The remaining solution concentration changed on treatment with different weights of activated carbon(AC), the high adsorption capacity as much as 942 mg g^{-1} was obtained. In addition, percentage removal of dissolved oil also increases with the increasing of carbon dose, and the maximum removal percentage of dissolved oil is 100 %, and according to Kuwait Convention and (Red Sea region) this minimum discharge limit of dissolved oil in produced water is 40 mg/l and 100 mg/l maximum (Kuwait R.C.,1979)**.**

4.2.3: Application of Freundlich model to dispersed oil adsorption

Data in table 4.3 presented in Fig 4.9, was found to fit Freundlich isotherm model and the constants k and 1/n are 2.47 and 0.1981 respectively were found as mentioned in the literature review is that $1/n < 1$. The position and slope of the isotherm line revealed the performance of the activated carbon, the representation of the experimental data by Freundlich equation resulted in a nearly linear curve with $r \approx 0.956$.

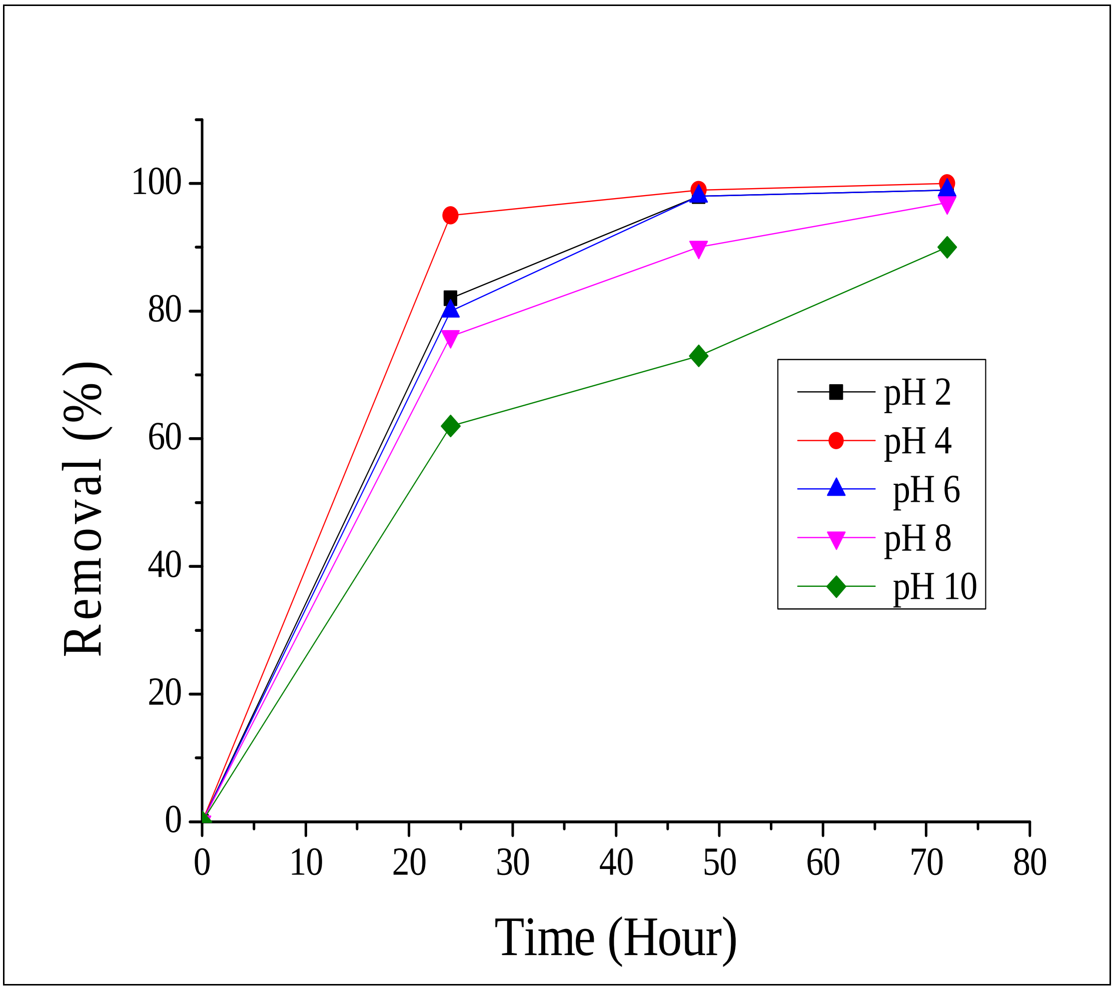

Fig. 4.7: The Effect of pH on dispersed oil removal

Table 4.3: Results of dispersed oil adsorption

Carbon Wt G	C_0 ppm	C_e ppm	Removal %	x/m	log Ce	Log x/m
0.0104	531	335	36.9	942.30	2.525	2.97
0.024	531	146	72.5	802.08	2.164	2.90
0.042	531	44	91.7	579.76	1.643	2.76
0.0604	531	4	99.2	436.25	0.602	2.63
0.081	531	0	100.0	327.77	0.000	2.51
0.1063	531	0	100.0	249.76	0.000	2.39

Generally higher isotherm line means that the carbon has better adsorptive capacity than the lower line and carbon that has a higher x/m value at a specified equilibrium concentration, which was 942 mg/g, will be preferred for treatment applications (US Environmental Protection Agency, 1973).

4.2.4: Determination of Zinc (+2) adsorption capacity

The effect of carbon dosage ranging from 0.0 to 0.12 g of the Activated carbon on Zinc (+2) solution (100 ml) with concentration of 120 g/l in table 4.4 is presented in Fig 4.10. The residual concentration changed on treatment with different weights of activated carbon (AC), adsorption capacity as much as 368 mg/g was obtained, the maximum removal percentage of Zinc (+2) is 88 %, (Bencheikh., 1989) obtained nearly similar results which was 90%.

4.2.5: Application of Freundlich model to Zinc (+2) adsorption

The data on Zinc (+2) adsorption was fitted to a Freundlich model and a graphical representation of this model showing the adsorption isotherms of AC on Zinc (+2) is shown in table 4.4 and presented in Fig 4.11, The constants k and 1/n were 1.25 and 0.5122 respectively were found, the position and slope of the isotherm line revealed the performance of the activated carbon, nearly linear curve with $r \approx 0.9731$. Generally, higher isotherm line means that the carbon has better adsorptive capacity than the lower line and carbon that has a higher x/m value at a specified equilibrium concentration, (US Environmental Protection Agency., 1973).

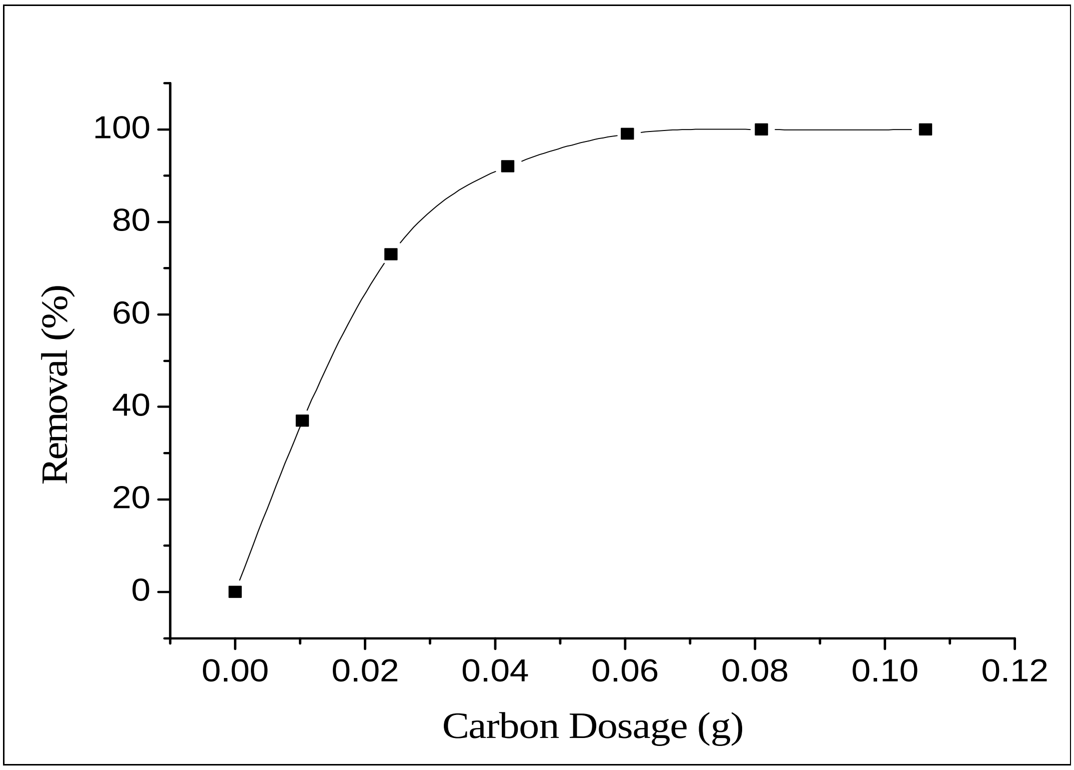

Fig. 4.8: The Effect of Carbon dose on Dispersed oil removal.

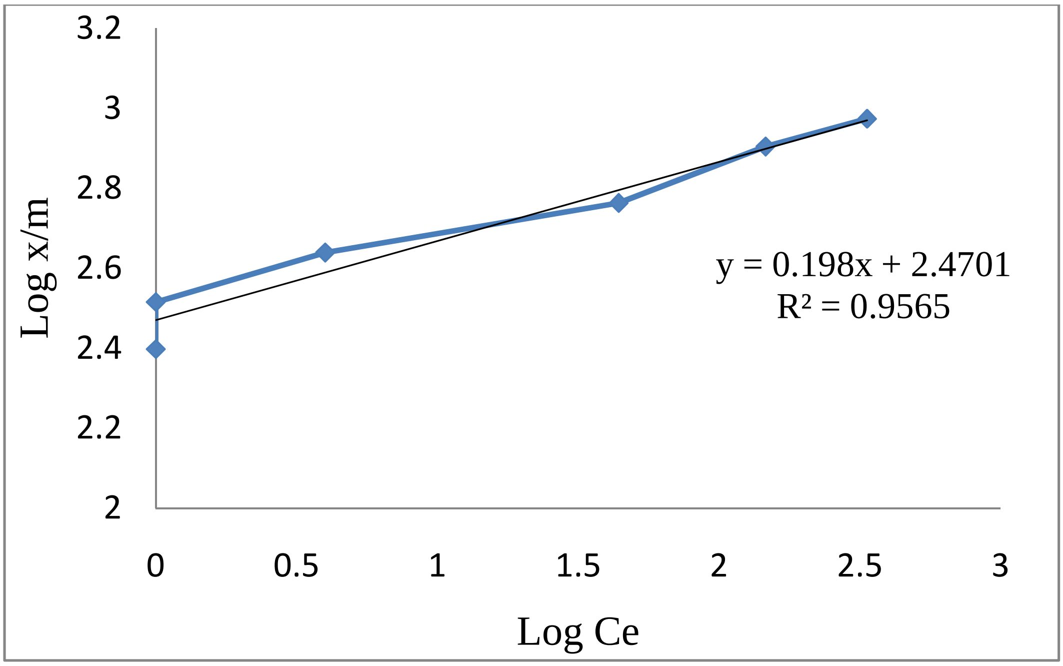

Fig. 4.9: Freundlich linear adsorption isotherm of dispersed oil.

Table 4.4: Zinc (+2) adsorption on AC.

Carbon Wt g	C_e ppm	Log C_e ppm	x/m	Log x/m	Removal %
0.0109	39.7	1.598	368	2.57	66.91
0.0323	35.86	1.554	260	2.42	70.11
0.062	23.96	1.379	154	2.2	80.03
0.094	16.73	1.223	109	2.0	86.05
0.1225	13.35	1.125	87	1.9	88.87

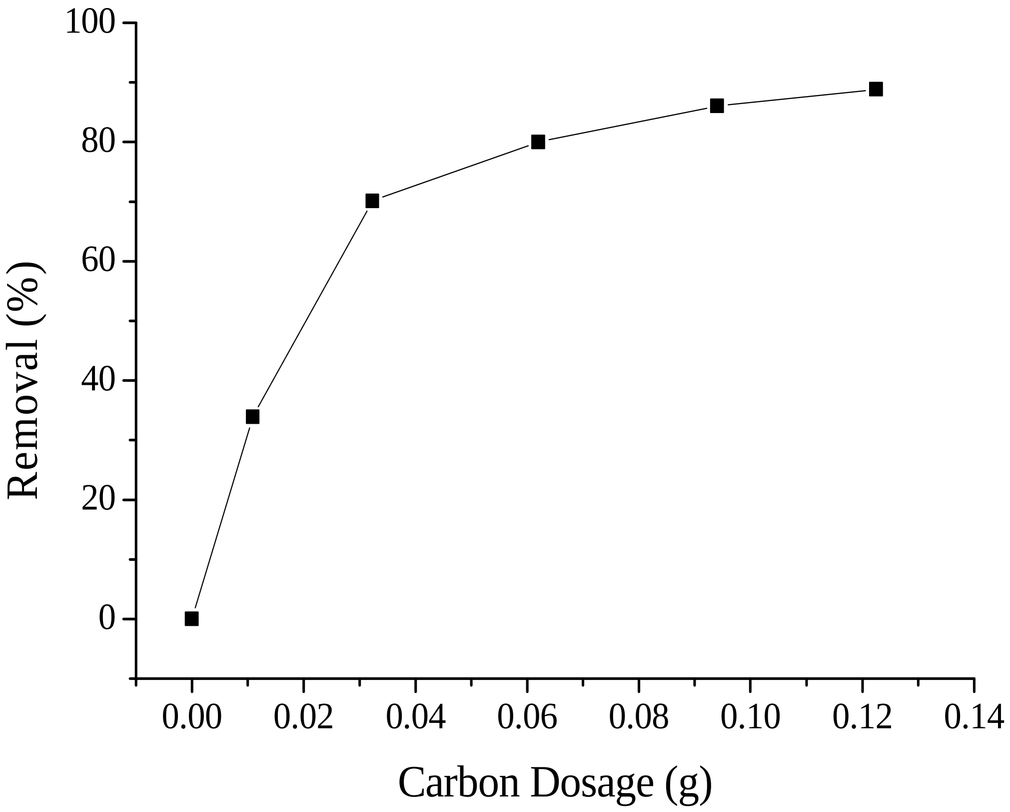

Fig 4.10: The Effect of Carbon dose on removal of Zinc (+2).

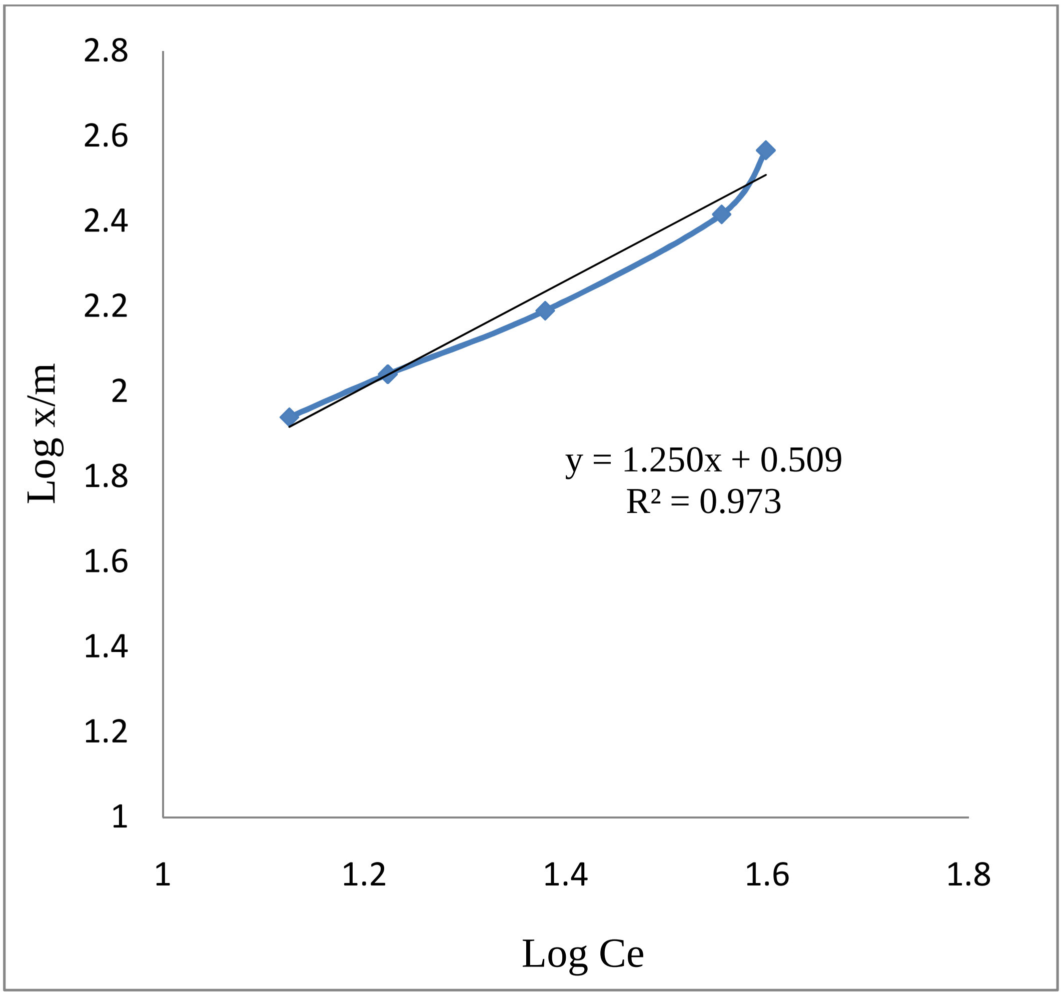

Fig 4.11: Freundlich linear adsorption isotherm of Zinc (+2).

5: Conclusions

- The results of this study show that, it is feasible to prepare activated carbons with relatively high iodine number (IN) and methylene blue (MB) from petroleum coke by direct chemical activation using potassium hydroxide (KOH) as activation agent.
- The iodine number (IN) and methylene blue (MB) of the prepared activated carbon(AC) increased with the increasing of the activation ratio (coke: KOH), reaching a maximum value of 1248.10 and 46.00 mg/g respectively with.
- The optimal conditions were found to be,1: 4 (coke: KOH) activating ratio, impregnation time of 2 h, activation temperature of 800 C and activation time of 1 h.
- The higher adsorption capacity of activated carbon (AC) towards the dispersed oil was (942 mg g^{-1}) at pH 4.
- Adsorption of dispersed oil fits Freundlich isotherm model with $r \approx 0.9565$ and the constants k and 1/n were 2.47 and 0.1981 respectively.
- Adsorption capacity of activated carbon (AC)toward Zinc (+2) is (368 mg/g).
- Adsorption of Zinc (+2) fits Freundlichisotherm model with $r \approx 0.9731$ and the constants k and 1/n were 1.25 and 0.5122 respectively.

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