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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM COFFEE WASTES

A graduation research project
submitted to the Department of Chemistry in partial fulfillment of the requirements
for the completion of the degree of Bachelor of Science in Chemistry

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First Semester, December 2015

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Dedication

I would like to dedicate my thesis to my beloved parents

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
CW	Coffee waste
CWAC	Coffee waste activated carbon
GAC	Granular activated carbon
AA	Activation agent
PAC	Powder activated carbon
Bicar	Sodium bicarbonate
FTIR	Fourier transform infrared spectroscopy
HCl	Hydrochloric acid
UV	Ultra Violet
MB	methylene blue
AcAg	activation agent

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Acknowledgements:

Praise and thanks to Allah to completing this work. And I would like to thank my supervisor Prof. Ammar Houas for patient supervision and guidance through this research, and dr.Lotfi Khezami for him kindly permission for using the (ASAP 2000) Micromeritics apparatus and the research laboratory . I also would like to thank the staff of the laboratories Dr. Abueliz Khalid and Babiker Yagoub for their help and cooperation .I have sincerely thank all my teachers during my colloge career. This work is done in department of chemistry.

ABSTRACT

The coffee waste is one of the most solid waste due to a large amount of waste generated from domestic and coffee shops. In this work, roasted coffee waste (CW) was employed as precursor for the production of carbons chemically activated with one of three activation agent (AcAg: KOH, ZnCl₂ and NaHCO₃). In a typical preparation the raw material was impregnated with (w/w)= 1/1 of CW / AcAg. The mixture was dried at 110°C for 24 h. The dried mixture was pyrolyzed at 750°C for 1h. The pyrolyzed material was washed with distilled water. The apparent and bulk densities, the pH, the moisture and the ash contents of the prepared activated carbons were determined. The CWAC were characterized by N₂ adsorption/desorption at 77 K and infrared spectroscopy (FTIR). The adsorption efficiency activated carbons were tested for the removal of the methylene blue dye from aqueous medium. In comparison with a commercial carbon, the activated carbons from coffee waste showed same and higher specific surface areas with values of 305.62 m²/g for CWAC KOH and 110.38 m²/g for CWAC Bicar. Both materials showed mainly micropores structure. Methylene blue removal capacity showed to be drastically higher than commercial product, with adsorption capacities of 404.54 m²/g and 237.92 m²/g for CWAC KOH and CWAC Bicar respectively.

Keywords: Activated Carbon , coffee waste , pyrolysis, ZnCl₂, KOH, NaHCO₃

المستخلص

تعد مخلفات القهوة واحدة من أكثر المخلفات الصلبة انتشاراً نظراً للكمية الكبيرة المستهلكة من محلات بيع مشروبات القهوة . وفي هذا العمل تم تحميص نفايات القهوة وتم استخدامها كمصدر أساسي لتحضير الكربون النشط كيميائياً مع واحدة من هذه العوامل المنشطة الثلاثة (هيدروكسيد البوتاسيوم , كلوريد الزنك و بيكربونات الصوديوم) . وفي تحضير الكربون النشط تم خلط المواد الخام (نفايات القهوة) مع العوامل المنشطة تبعاً للوزن 1/1 لكل من نفايات القهوة / العامل المنشط . ومن ثم تم تجفيف الخليط عند درجة حرارة 110 درجة مئوية خلال 24 ساعة . وبعد ذلك عمل تحليل حراري للخليط المجفف عند درجة حرارة 750 درجة مئوية لمدة ساعة. و من ثم غسل الخليط بالماء المقطر . وتم حساب كلاً من الكثافة الظاهرية والحقيقية , الأس الهيدروجيني , الرطوبة والرماد للكربون النشط المحضر . وتمت دراسة وتوصيف خصائص الكربون النشط المحضر من نفايات القهوة باستخدام جهاز الإدمصاص بغاز النيتروجين عند درجة حرارة 77 كلفن وجهاز مطيافية الأشعة تحت الحمراء . كفاءة الإدمصاص للكربون النشط تم تجربتها على إزالة صبغة أزرق الميثيلين من الوسط المائي. وبالمقارنة مع الكربون النشط التجاري , أظهر الكربون النشط المحضر من نفايات القهوة قيم مشابهة للكربون التجاري وقيم أعلى منه لمساحة السطح الخاصة حيث قيمة مساحة السطح تساوي 305.62 متر² / جرام للكربون النشط المحضر باستخدام هيدروكسيد البوتاسيوم و 110.38 متر² / جرام للكربون النشط المحضر باستخدام بيكربونات الصوديوم . وبشكل أساسي أظهرت احجام جميع المسامات للمواد المحضرة بحجم المايكرو. وتميز الكربون النشط المحضر من نفايات القهوة بسعة استيعاب عالية لإزالة صبغة أزرق الميثيلين مقارنة بالكربون النشط التجاري مع سعة إدمصاص يساوي 404.54 متر² / جرام و 237.92 متر² / جرام للكربون النشط المحضر باستخدام هيدروكسيد البوتاسيوم و للكربون النشط المحضر باستخدام بيكربونات الصوديوم على التوالي .

الكلمات المفتاحية : الكربون النشط , نفايات القهوة, تحليل حراري , هيدروكسيد البوتاسيوم , كلوريد الزنك , بيكربونات الصوديوم.

Chapter 1

Introduction

Background of study:

Activated carbons (ACs) is wide commonly used as adsorbents of the industrial pollutants: organic compounds, heavy metals, herbicides, dyes, and many others toxic and hazardous compounds. They are used for water treatment and air pollution control in the environmental field but also for many other applications such as decolorization of sugar etc. It has high adsorption capability due to its high surface area and porosity formed during carbonization process. Activated carbons produced by either physical or chemical activation processes using gases and chemical compounds solid or in solution. The presence of these agents and carbonization conditions have play role on the development of pore structures, surface area surface functional groups, etc. [1]. During activation, there is two steps carbonized raw materials and activated carbonized of raw materials in first step the carbonization temperature range from 400 to 850 °C and second step activated carbonization using water vapor , carbon dioxide or mixed of carbon dioxide and water vapor at temperature between 600 c° and 900 c° . In chemical activation , the precursor materials impregnated with chemical activation agents such as alkali , alkali earth salts and acids (KOH, NaOH, NaHCO₃, ZnCl₂, H₃PO₄ and H₂SO₄ ,) the chemical agents play role as dehydrating agents and oxidants then carbonized the mixture at high temperature in inert atmosphere (pyrolysis process) then washing to remove the residue of chemical agents and some ions ..The precursor materials for produced activated carbons are mainly from carbonaceous materials or lignocellulosic materials. The advantage for using the lignocellulosic materials like agricultural by-product or waste such as coffee wastes precursor are generated from agricultural wastes and it's has low cost , readily available and conversion the wastes into valuable materials .The can be used to produced the activated carbon with high specific area [2]. Some researchers have been reported for preparing activated carbon from these type of materials such as shells of Macore fruit [3] , Macadamia nutshell [4] , coir pith [5]. The coffee wastes.

Objectives of the study:

The objective of this study is to use a cheap and available abundant carbon precursor (conversion the wastes into a valuable materials) and new unusual activation agent amphoteric NaHCO₃ to produce high specific surface area activated carbon using a chemical activation method coupled with high temperature treatment under inert atmosphere.

Scope of the study :

In this study, waste coffee was used as raw material to obtain activated carbon adsorbent using two-step physicochemical activation method. Preparation was carried out in a horizontal cylindrical muffle furnace. Three substances were selected as chemical agents in the impregnation procedure: Potassium hydroxide (KOH) and Zinc chloride ($ZnCl_2$) because they were found to be very effective as chemical agents in creating porosity in activated carbons and sodium bicarbonate ($NaHCO_3$) because it never be used in the preparation of activated carbon. Whereas, the inert argon gas was used in the activation.

For preparatory conditions a fixed activation temperature ($750\text{ }^\circ\text{C}$), impregnation ratio of AcAg/char (1) and Argon pyrolysis time (1 h) were selected based on the literature review. The prepared activated carbons were also characterized by using Micromeritics ASAP 2000, to determine the specific surface area and the porosity of the prepared activated carbons.

The methylene blue adsorption was used to determine the performance of activated carbon adsorbent. The effect of initial concentration of adsorbate (100-500mg/L) and contact time (48 h) were carried out in the adsorption study.

Part 1
Literature Review

Introduction:

The first carbon adsorption experiments were carried out by Schele in 1773. After this time the use of activated carbon is greatly diversified especially in the removal of impurities in the liquid phase. Since 1930 the activated carbon is used for the processing and production of water for drinking. The discovery of the adsorption phenomenon is much more recent and has greatly helped to expand and enhance its use. Its application on industrial scale was achieved some years later when the charcoal was used in a refinery to bleach cane sugar (6). In early 20th century adsorption techniques have undergone a remarkable development through scientific knowledge gathered in the field of adsorption. Activated carbon is routinely used in the pharmaceutical, petrochemical, chemical and especially in the field of water treatment as well as waste water destined for human consumption. It is also recognized that the porosity and the adsorption capacity is the most influence on the adsorption of organic compounds on active carbon settings. Thus the choice of raw material and the activation process are very important for obtaining a material having a large specific surface area and a specific porosity.

1.1. Activated carbon (AC):

The porosity within activated carbon which imparts their dominant characteristics of adsorption. Activated carbons are prepared from a wide range of carbon types (the family of carbons) of different structures. As porosity and structure are so intimately related, an understanding of the structures in this range of carbons together with a description of their origins and preparation are prerequisites to the effective use of activated carbons.

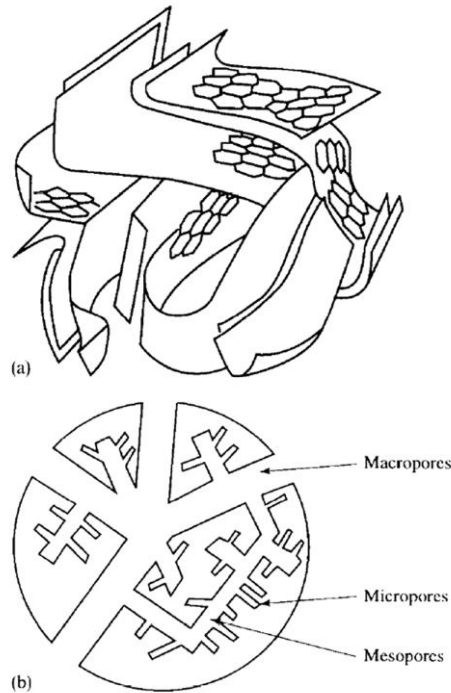


Figure.1.1. (a) Schematic representation of the structure of activated carbon (adapted from Ref. [7]); (b) schematic representation of an activated carbon granule [8].

1.1.1. Characteristics of Activated carbon:

Surface area:

Activated carbons are widely used because of their high specific surface area and their well developed porosity. Specific surface area values are usually from 500 m²/g to 3000 m²/g and can be explained by the micropore structure. At first sight, it seems that for a higher surface area, the adsorption characteristics as adsorbent will be better because there will be more points where the adsorbed molecules (adsorbate) could be retained. However, depending on whether the adsorbate molecules size is bigger than some of the micropore size not all surfaces will be available for those molecules. At the same point the geometry of the adsorbate and the pore have to be taken into consideration as well.

1.1.2. Properties of Activated carbon:

Activated carbon products can be characterized by its activity and physical properties. Activity properties include pore size distribution that defines the available pore volume of a carbon over three pore size regions: the micropore, mesopore, and macropore regions. Micropore region - less than 2 nm, Mesopore region - between 2nm - 50nm and Macropore region - greater than 50 nm ,Physical properties include surface area, product density, and ash content .

1.1.3. Raw Materials of Activated carbon (AC):

Many carbonaceous materials can be used as raw material for activated carbon fabrication such as agricultural residues: coco nut shell, corn cobs, sugar beet leaves, rice straw and cotton stalks [9].

1.1.4. Applications of Activated carbon:

About 60% of the production of commercial activated carbons are obtained from coal (10). Many different industries use very important quantities to the removal of pollutants. Furthermore, activated carbons are multipurpose adsorbents because they can be used in so many sectors basically due to their large surface area which confers them a high capacity for adsorbing chemicals from gases or liquids. However, the properties of the activated carbons largely define their applications.

Two forms of AC can be used both in liquid or gaseous media, as powder (PAC) or granular (GAC) form. In general, PAC is used in liquid media while the GAC can be applied in both media.

Activated carbons are mainly used in liquid phase for water treatment to remove compounds that affect taste, odor, color, chemicals and bacteria. The food industry is also one of the big consumers for the same purposes. In the biomedical field, activated carbons can be applied for purification of proteins or in the separation of metallic compounds as gold and silver, but also have medical purposes as purification of blood plasma.

- In gaseous phase, their applications are the storage and separation of gases. They can be found in radioactive protection in nuclear plants, in food industries for deodorization and have perspectives as catalyst support and catalyst too.

Activated carbons are required in many industries for the treatment of waste water and gaseous effluents to meet environmental regulations and for material recovery purposes as well as for example for separation of hydrogen sulfide from air [11].

1.2. Coffee waste (Coffee grounds):

After drinking a cup of coffee, there is always coffee grounds in the cup or machine. Instead of throwing it, there are some solutions "recycling" to use it well!

- What coffee grounds?

Coffee grounds is this residual powder that remains at the bottom of the cup ... Made up of fine-grained, granular, it is a component of many recipes and tips grandmother. It is advisable to let it dry before using. Here are some amazing treatments and cures based coffee grounds!

- Coffee grounds: an invigorating hair care:

Your hair is dry and need a little care? Use coffee grounds to make a mask to your hair. The technique is very simple: before applying your usual shampoo, wet your hair with coffee grounds and leave for a few minutes. Then, make your shampoo. You will be amazed by the brilliance of your hair! This recipe is recommended for blondes, as it can darken their hair.

- Coffee grounds: to restore radiance to your wood furniture:

To restore radiance to your old wooden furniture, put coffee grounds in water and then brush your furniture. Let the product a few minutes and wipe with a cloth.

- Coffee grounds: a natural fertilizer:

Another use that you had no idea! Apart from its repellent to insects, coffee grounds is a very effective natural fertilizer that helps make the most fertile soils and improve the health of your plants.

- Coffee grounds enables it to fight against global warming?

That's what has just announced a group of scientists ... According to a study published in the journal Nanotechnology, researchers announced recently (September 2015) they could store methane in the coffee grounds. A solution that would reduce the emission of greenhouse gases and to improve waste recycling.

How is this possible ? By soaking the coffee grounds in sodium hydroxide and heating at 900 ° C. The important point of this study is that coffee grounds can turn toxic gas and pollutant source of energy that can slow global warming

The coffee is almost the most consumed drink in the world thus, it is produced all over the world and in great quantities, which means a great amount of residues generated that must be treated properly.

As can be seen in the figure.1.2., the minimum coffee consumed in Oman for example is 1 kg per person per year. Since, Oman population is 4,092,000 persons, so approximately 40,920 tons of coffee ground is to be rejected per year only in this country which can transformed. A part of these coffee grounds were recycled into soil remediation materials or adsorbents for odour removal after been carbonized (12) .

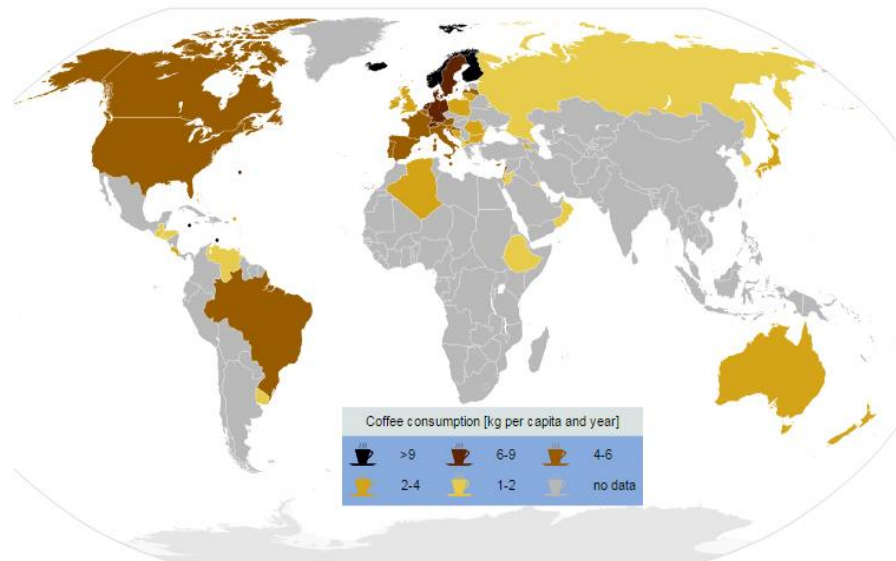


Figure1.2. Coffee consumption map around the world (13).

1.3. Physical activation for activated carbon:

Physical activation is often carried out at a relatively high temperature between 750 °C and 1000 °C, where the biomass is in contact with a weakly oxidizing gas such as steam, CO₂, or a mixture of these gases. This activation process results in the preparation of an activated carbon with narrow pores and is limited by the transport of oxidant gas into the solid. In this type of process, the temperature control is an important parameter: dissolved 800 °C, the reaction rate is too slow and economically uninteresting higher than 1000 °C the reaction erodes the material whose size considerably reduced while the interior the char remains inactivated.

1.3.1. Pyrolysis temperature :

The temperature level plays an important role in the activation process. Indeed, at low temperatures, the oxidation kinetics is low and the activation leads to a homogeneous pore size distribution throughout the volume of the material. When the temperature increases, the reaction rate increasing faster than the diffusion of the oxidizing gas. The method is therefore limited by the transport of the oxidizing gas within the material, which leads to a loss of homogeneity of the porosity.

1.3.2. Pyrolysis duration:

This parameter can affect the yield percentage of the final product. It must be optimized to obtain the maximum porosity development without decreasing too much the production yield due to an excessive combustion. Bouchelta et al. (2008) (14) have shown that the yield

percentage decreases with increase of activation temperature and hold time. Carbonization times ranging from 1 h up to 14 h (15) have been used in charcoal production.

1.3.3. Pyrolysis atmosphere:

Pyrolysis atmosphere is usually an inert gas, such as N₂ or Ar. Its role is to favor the development in the carbon's porosity. Thus, the flow and the gas type may affect the final properties of the activated carbon. For example, CO₂ flow-rate had a significant influence on the development of the surface area of oil palm stones (Lua & Guo, 2000)(16).

1.4. Chemical activation:

In the chemical activation method for activated carbon preparation, the carbonaceous material is carbonized after the addition of a concentrated solution of highly oxidizing agent which minimize the formation of tar. Chemical agent is also used to recover reuse, to free the pores after carbonization and to obtain a carbonized product with very good sorption properties in a single step.

Chemical activation is used almost exclusively for carbons produced from lignocellulosic materials. The activation agent influences the pyrolytic process such for example: tar amount restriction to a minimum, accordingly increasing the yield of carbon in the carbonized product. Furthermore, temperature needed for pyrolysis is also lower than that needed for activation with gaseous agents in physical activation, and this promotes the development of a porous structure. Under these conditions elementary crystallites of smaller dimensions, (micropores) are formed (Balci, 1992) (17) the most widely used activation agents are H₃PO₄, ZnCl₂, KOH and K₂S. In some studies hydroxides of an alkali metal, magnesium and calcium chloride and other substances are also used. All these chemicals are strong dehydrating agents. On calcination, the impregnated chemicals dehydrate the raw materials, which results in changing and aromatization of the carbon skeleton by the creation of a porous structure and surface area.

1.4.1. Activation agents:

The activation agents use as dehydrating agents and oxidants, and the common activating agents its used is (KOH, ZnCl₂, H₃PO₄) [18].

- The inorganic compound activation agent KOH is a strong base and is used in many industrial applications. Some of its characteristics are its high reactivity toward acids and its corrosive nature. Several authors studied the effects of KOH on carbonization of carbonaceous materials (19, 20, 21). Thus, the preparation of active carbons were made from starting materials poor in volatiles and a high content of carbon as petroleum cokes, metallurgical coke and charcoals from wood.

- ZnCl_2 was employed in the 1970's especially for wood wastes. However, it is no longer used due to the environmental problems that generate. Impregnation with ZnCl_2 produces a degradation of the cellulosic material, during the carbonization results in charring and aromatization of the carbon skeleton and creation of the pore structure (22).

1.4.2. Ratio (activation agent/ raw materials):

This parameter is an important factor in chemical activation is the degree of impregnation. It is also defined as the coefficient of impregnation. It has an apparent and direct effect on the porosity of the resulting product. Indeed, the volume of salt in the carbonized material is equal to the volume of pores, which are freed by its extraction. For small degrees of impregnation, a small increase in impregnation amount causes an increase in the total pore volume of the product showing an increase in the volume of smaller pores. When the degree of impregnation is further raised, the number of larger diameter pores increases and the volume of the smallest pores decreases.

For example, the raw material and the chemical are mixed in an aqueous solution in ratios KOH: precursor between 2:1 and 4:1. After the reaction it is burned off at the range of 700–900°C in an inert atmosphere. It can make the oxygen of the alkali remove cross-linking and stabilizing carbon atoms in crystallites whereas K metal may be intercalated. Removal of potassium salts, by washing, and carbon atoms from the internal volume of the carbon, by activation reaction, create the microporosity of the activated carbon in the new structure.

Part 2

Experimental

2. 1. Materials and Methods:

2.1.1. Chemical and reagents:

Experiments were conducted to produce activated carbon from coffee residues and the equipment used is listed:

1. Oven.
2. Beaker.
3. Drop by drop washing system.
4. Furnace.
5. ASAP 2000. Surface area and porosimetry system.
6. UV-visible Spectrophotometer for MB analysis.

The chemicals involved in the preparation of activated carbons have been the following :

- Deionized water.
- Potassium hydroxide KOH. Used in the chemical activation.
- Zinc chloride $ZnCl_2$. Used in the chemical activation.
- Sodium bicarbonate. Used in the chemical activation.

Physicochemical properties of these activation agents are listed in the table 2.1.

- Methylene blue MB. Used to evaluate the adsorbability of the prepared activated carbons and to determine the apparent surface area.

2.1.2. Preparation of the activated carbons (CWAC) procedure:

The coffee waste (CW) was impregnated with one of activation agents (AcAg) $ZnCl_2$, $NaHCO_3$ and KOH with $w(AcA):w(CW)$ ratio of 1:1. A volume of 500 mL of distilled water were added to the mixture (CW+ Ac Ag) and the solution was stirred for 1hour in magnetic stirrer at the maximum speed. The pH for solution was measured and the solution was washed by distilled water and dried at 110 °C for 24 hours. The dried solid mixture was carbonized at 750 °C during 1 hour under inert atmosphere (Argon gas) with a (Ar) flow rate of 20 L/h and heating rate equal to (10 °C/min). The formed activated carbon was then cooled under (Ar) gas flow to the room temperature.

According to nature of activation agent the prepared activated carbon was symbolized by **CWAC $ZnCl_2$** , **CWACKOH**, **CWACBicar** and **CWACPhys** for the activated carbon prepared in the same thermal condition but without chemical activation.

All activated carbon were neutralized to a pH around 6-8 by distilled water using a drop by drop system.

Table 2.1 Some physico-chemical properties of the used activation agents.

Chemical formula	ZnCl ₂	KOH	NaHCO ₃
Molar mass	136.315 g/mol	56.11 g/mol	84.0066 g/mol
Appearance	white crystalline solid hygroscopic and very deliquescent	white solid, deliquescent	White crystals
Odor	odorless	odorless	odorless
Density	2.907 g/cm ³	2.044 g/cm ³ (20 °C) 2.12 g/cm ³ (25 °C)	2.20 g/cm ³
Melting point	290 °C (554 °F; 563 K)	360 °C (680 °F; 633 K)	50 °C (122 °F; 323 K) (decomposes to sodium carbonate)
Boiling point	732 °C (1,350 °F; 1,005 K)	1,327 °C (2,421 °F; 1,600 K)	9 g/100 mL 69 g/L (0 °C) 96 g/L (20 °C) 165 g/L (60 °C) 236 g/L (100 °C)
Solubility in water	432.0 g/L (25 °C)	85 g/100 g (-23.2 °C) 97 g/100 mL (0 °C) 121 g/100 mL (25 °C) 138.3 g/100 mL (50 °C) 162.9 g/100 mL (100 °C)	0.02 %wt acetone, 2.13 %wt methanol at 22 °C. insoluble in ethanol
Solubility	soluble in ethanol, glycerol and acetone	soluble in alcohol, glycerol insoluble in ether, liquid ammonia	-0.82
Solubility in alcohol	430.0 g/L	55 g/100 g (28 °C) ~14 g / 100 g (28 °C) 13.5 (0.1 M) 1.409 (20 °C)	10.329 6.351 (carbonic acid) 1.3344

Figures 2.1 and 2.2 show two schematic of the preparation procedure.

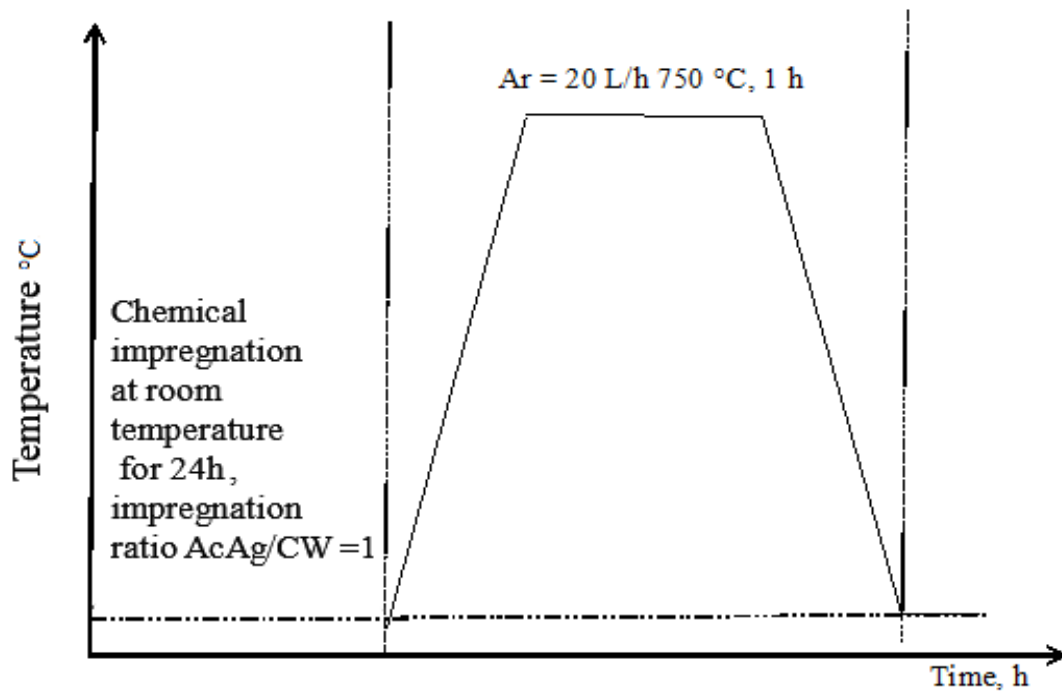


Figure.2.1 Diagram of the experimental of prepare the AC set up.

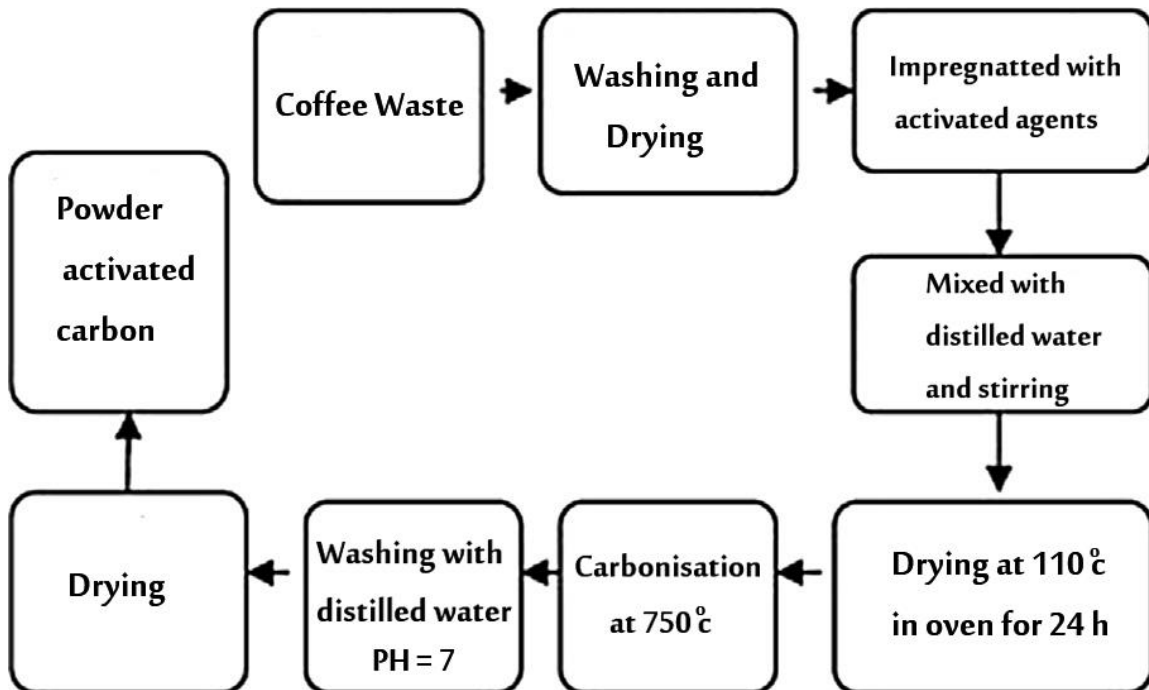


Figure. 2.2. Schematic for the preparation of A.C from C.W .

Figure.2.3.The experimental apparatus used is shown in

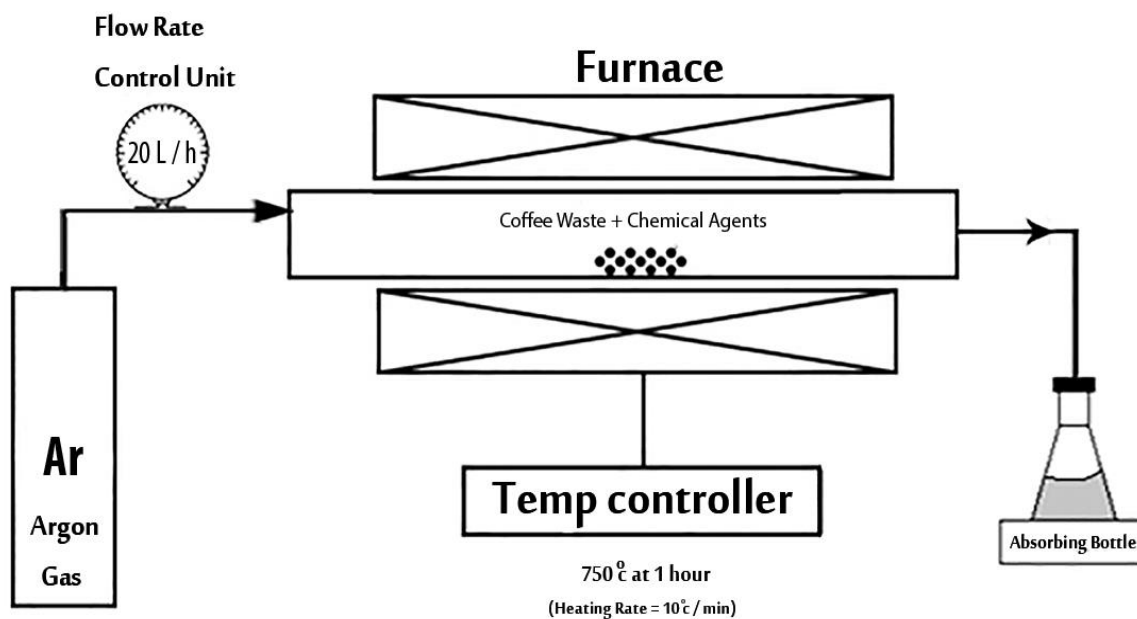


Figure.2.3. Laboratory schematic experimental set up used for the AC preparation

2.2. Characterization of Activated carbon:

2.2.1. pH Value determination :

For the pH of prepared activated carbons determination, an amount of 2 g of activated carbon was added to 100 mL beaker containing 50 mL of distilled water. The suspension was heated to make it CO₂ free. ,the mixture was cooled at room temperature and measured the pH for it.

2.2.2. Relative density:

Relative density of activated carbon was determined by dividing its mass by the water it displaces. The water was added in graduated cylinder and the volume was measured in (cm³) , then 0.5 ~ 2 g of activated carbon were added to a graduated cylinder with water and volume was measured in (cm³). The relative density was calculated as follows:

$$ds = m / (V_2 - V_1) \quad \text{Eq.2.1}$$

ds: true density (g/cm³)

m: Activated carbon mass (g)

V₁: volume of the water without activated carbon (cm³)

V₂: volume of the water with activated carbon (cm³)

2.2.3. Bulk density:

Apparent or bulk density of activated carbon was determined by filling a graduated cylinder with activated carbon and the volume was measured as (cm³). , then the mass of activated carbon was calculated. The bulk density is calculated by the following formula:

$$d_{app} = (m_2 - m_1) / V \quad \text{Eq.2.2}$$

d_{app} : Apparent density (g/cm³)

m_1 : mass of the graduated cylinder empty (g)

m_2 : mass of the graduated cylinder with activated carbon (g)

V : volume of the activated carbon (cm³)

2.2.4. Moisture content :

The moisture content of activated carbon was determined by activated carbon mass difference before and after drying in an oven, (1g) of activated carbon was placed in an oven at a temperature of 150 ° C for 3 hours. The weight of activated carbon before and after drying were calculated .The percentage of moisture content was calculated as follows:

$$\text{Moisture content (\%)} = [(M_0 - M_1) / M_0] * 100 \quad \text{Eq.2.3}$$

M_0 : the initial mass of coal (g)

M_1 : mass of coal after drying (g)

2.2.5. Ash content :

Ash content was determined by the same method as done in moisture content except the temperature at 750 ° C . ash content was calculated as follows :

$$\text{Ash content (\%)} = (D/B) \times 100 \quad \text{Eq.2.4}$$

Where

D = Wight of residue left in gram

B = weight of dried sample in gram

2.2.6. Methylene blue adsorption:

Experimental procedure: Methylene blue adsorption tests were measuring by mixing 0.1 g of each, prepared activated carbon and commercial activated carbon separately with 100 ml of 10 to 300 (mg/0.1 L) methylene blue solution. After shaking for 48 hours, the suspensions were

centrifuged and diluted between 10 to 50 times before analysis. Methylene blue residual concentration (C_e) was measured at 665 nm using an UV /Vis spectrophotometer. Linear Beer-Lambert relationship was used for the determination of concentration.

Modeling: Some carbon have mesopores structure which adsorb medium size molecules such as dye Methylene blue. Methylene blue was chosen in this study because of its known strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material.

Principle: The Langmuir equation was used to calculate the specific surface area of the sorbents. The general form of Langmuir isotherm is as:

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \quad \text{Eq.2.5}$$

where

C_e : Equilibrium methylene blue solution concentration (mg/L)

q_e : amount of adsorbed methylene blue molecules at equilibrium (mg/g)

q_{\max} : Maximum amount of adsorbed methylene blue molecules at the monolayer (mg/g)

K_L : Langmuir thermodynamic equilibrium constant (L/mg)

Experimental data obtained were fitted with the software Origin.7 by the Langmuir model to determine q_{\max} and K_L .

2.2.6. Apparent surface area determination:

The apparent surface area was calculated by equation:

$$S_{MB} = (N_g \times a_{MB} \times N_A \times 10^{-20}) / M_{MB} \quad \text{Eq.2.6}$$

where

- S_{MB} is the apparent surface area in m^2/g ;
- N_g is the amount of methylene blue adsorbed at the monolayer of sorbents in mg/g
- a_{MB} is the occupied surface area of one molecule of methylene blue = 197.2 \AA^2 (Graham, 1955)
- ;
- N_A is Avogadro's number = $6.02 \times 10^{23} \text{ mol}^{-1}$ and
- M_{MB} is the molecular weight of methylene blue = 373.9 g/mol

2.2.7 Procedure of analysis by N₂ adsorption- desorption:

A commercial volumetric gas adsorption apparatus "ASAP 2000", Accelerated Surface Area and Porosimetry System manufactured by Micromeritics Co., USA was used to measure the surface area and to determine the pore size distributions of mesopores using N₂ adsorption data at -195.6 °C.

To measure the mesopore surface area and the mesopore volume of the samples nitrogen gas adsorption and desorption isotherms were obtained at - 195.6 °C. For each experimental point, an equilibration time of about 30 minutes was allowed. The cross sectional area of the nitrogen molecule was taken as 0.162 nm² (23). Surface area of the samples was determined by using BET equation in the relative pressure range of between 0.05 to 0.35 over twenty adsorption points. The area and the volumes of the pores as well as their distributions were evaluated from the nitrogen adsorption isotherms using the Barrett, Joyner and Halenda (BJH) method (24) considering the IUPAC mesopore range definition which ranges from 50 nm down to 2 nm in terms of the pore diameters of the cylindrical shaped pores.

2.2.8 Infrared spectroscopy (FTIR):

The study-infrared spectroscopy (in transmission) activated carbons allows the determination of all surface features by identifying functions from changes induced during processing solid and surface reactions (25).

However, this characterization technique in the case of activated carbon has some disadvantages:

- Coal being black coloring, it adsorbed much energy.
- The interpretation of the spectra is difficult because of the overlap of absorption and low signal intensity due to active carbon black character strips.
- The identification of functional groups remains complicated because it is difficult to consider that each groups is isolated as in the case of organic chemistry.

In most published research within characterization of activated carbon infrared spectrum analysis shows (26).

Part 3

Results and Discussion

Introduction :

The precursor elemental composition, shown in Table 3.1, reveals that the coffee waste raw material used is composed mainly of carbon, oxygen and hydrogen, as can be expected in most lignocellulosic materials. The ashes are composed mainly of potassium, calcium and magnesium which can catalyse the reactions involved in the activated carbon production and lead to higher reactivity towards activation and higher rates of activation (27).

Table 3.1. Raw material (Coffee waste) elemental composition

Coffee Waste	Elemental composition/ wt.%				
	O	C	H	N	S
	37.7	46.3	6.4	2.7	0.3

3.1. Physical Characterization:

A physical characterization of the prepared activated carbons produced from coffee wastes was carried out.

3.1.1. Weight loss, yield and ash contents determination :

During the manufacturing step analyses have been made on the weight losses after activation process which are shown in the table 3.2.

The obtained percentage weight loss was found to be in the range of 60 - 71% which represents a yield percent varying from 30 to 40 %. The highest yield was found for the CWAC KOH due to the fact that CWAC KOH has the highest ash content (Table.3.3) indicating probably the highest amount of inorganic oxides in the structure.

On the other hand, activated carbon yields do not show a huge relevant changing tendency, from an activation agent to another. However, sample impregnated with KOH solution shows higher yield compared to the values obtained of the samples impregnated with the three other AcAg at the same carbonization temperature which have very similar yield percentages.

Table.3.2. Weight loss of the prepared activated carbons

Activated carbon	Weight before calcination (g)	Weight after calcination (g)	Weight loss (g)	Weight loss %
CWAC ZnCl₂	29.52	8.61	20.91	70.84
CWAC Bicar	24.60	7.48	17.11	69.55
CWAC KOH	35.71	12.12	23.58	60.04
CWAC Phys	44.64	13.74	30.89	69.21
Commercial A.C	-	-	-	-

Table.3.3. Yield and ash contents of the prepared activated carbons

Activated carbon	Yield %	Ash content %
CWAC ZnCl₂	29,16	3.78
CWAC Bicar	30,45	9.28
CWAC KOH	39,96	37.07
CWAC Phys	30,79	3.85
Commercial A.C	-	-

3.1.2. Moisture contents determination :

Activated carbon produced from coffee waste can be a perfect adsorbent material for harmful substances including organic vapors due to its outstanding adsorption capacity and cost advantage. However, moisture adsorption of the carbon generally decreases the adsorption capacity for organic vapors. As shown in the table 3.4., the moisture content drastically decreases for all activated carbons except for CWAC Bicar, indicating an increase in the adsorbability of the AC compared to their raw materials.

Table 3.4. Moisture contents of the raw coffee waste and the prepared activated carbons

Activated carbon	Moisture content directly drying %	CW Chemically activated	Moisture content directly drying %
CWAC ZnCl₂	9.40	CW ZnCl₂	20.24
CWAC Bicar	12.96	CW Bicar	14.41
CWAC KOH	7.80	CW KOH	19.75
CWAC Phys	0.73	CW	26.43
Commercial A.C	-	-	-

3.1.3. pH, densities and porosity:

AC Slurry pH is an indicator of nature of the surface functional groups of activated carbon because, they give an idea about the presence and absence of oxygen or hydrogen containing functional groups. Also pH of the solution influences the adsorption process by changing behaviour of the adsorbate-adsorbent interactions significantly.

As it was shown in table3.5. all the activated carbons produced had slurry pH in the range of 8 - 11. It seems that chemical activation made these products from slightly to really basic. The amount and nature of the basic surface functional groups of products caused differences in pH values.

Table.3.5. pH, densities and porosity of the prepared activated carbons.

Activated carbon	pH	Real density (g/cm ³)	Apparent density (g/cm ³)	Porosity %
CWAC ZnCl ₂	7.9	0.85	0.45	47.37%
CWAC Bicar	10.1	1.18	0.62	48.22%
CWAC KOH	10.7	0.80	0.53	33.75%
CWAC Phys	9.88	0.47	0.31	34.04%
Commercial A.C	9.9	-	-	-

3.2 Adsorption properties:

After these steps surface area (BET), pore volume, pore diameter and pore distribution were analyzed.

3.2.1 BET surface area:

Figures 3.1. shows the N₂ adsorption / desorption isotherms of the prepared activated carbons. Isotherm shapes in the literature which were originally defined by Brunauer et al. (1943) and classified into 6 well-known groups, it is clear that all products show similar isotherms to the type I. According to Brunauer, this type of isotherm is observed in the case of microporous solids. Another way of obtaining information on the porous texture of the solids is to compare the shape of the hysteresis loop with the shape of adsorption and desorption branches of the standard shapes which were originally classified by De Boer (1958). But, as it is shown in the isotherm figures of the samples, there is no distinct hysteresis loops at adsorption / desorption isotherms.

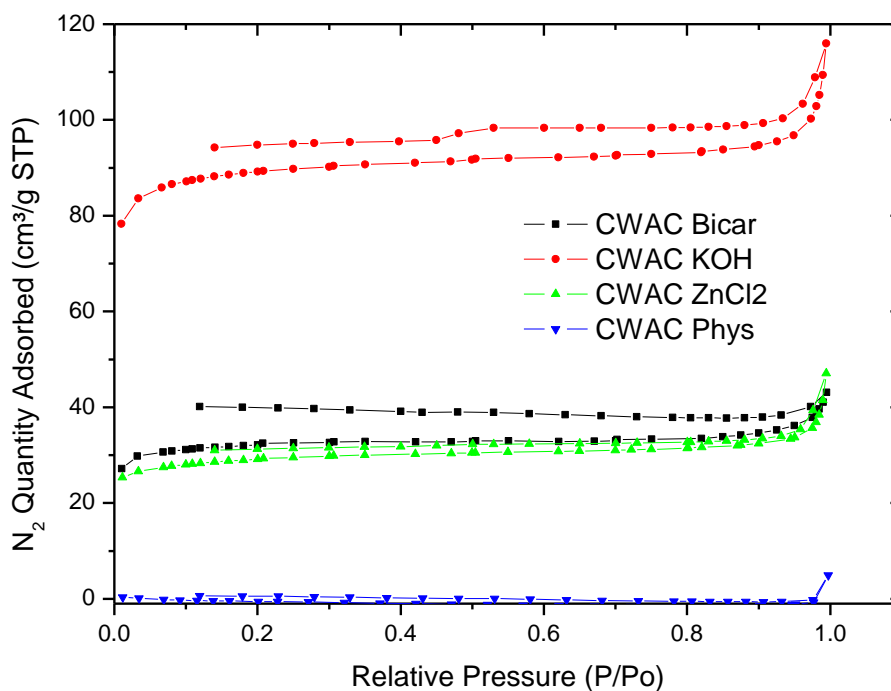


Figure 3.1. N₂ Adsorption/Desorption Isotherms of prepared activated carbons

In Figure 3.2, BET surface areas of prepared activated carbons are shown. CWAC Phys sample, without any impregnation and carbonized at 750 °C under Ar atmosphere for 1 h, had the lowest surface area 0.463 m²/g. The highest BET surface area was obtained for the sample impregnated with KOH solution and carbonized at the same conditions, as 305.62 m²/g (CWAC KOH).

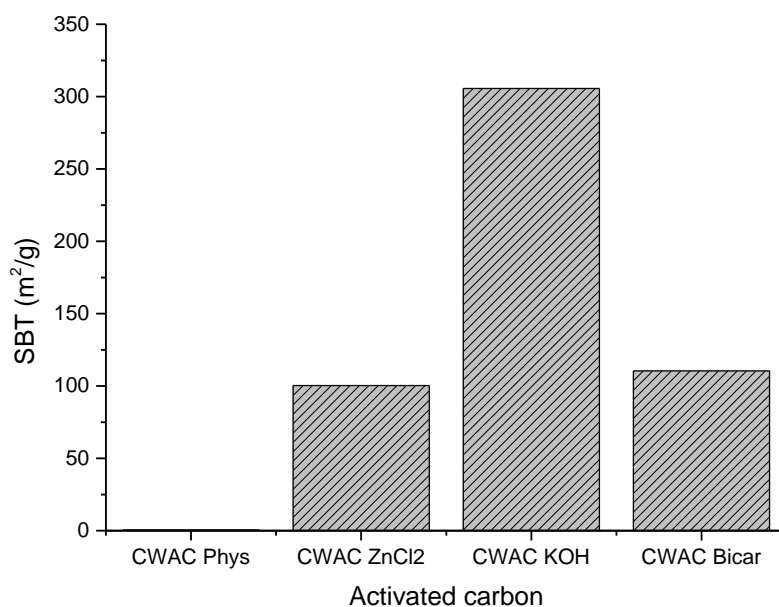


Figure 3.2. BET specific surface areas of prepared activated carbons.

3.2.2 Methylene blue adsorption:

MB adsorption isotherms on the prepared activated carbons are shown in the figure 3.3. Because of the difference of adsorption capacity they have been separated in two figures (a) and (b). CWAC Phys and CWAC ZnCl₂ have the lowest adsorption capacities, while the highest MB adsorption has been found with the CWAC KOH.

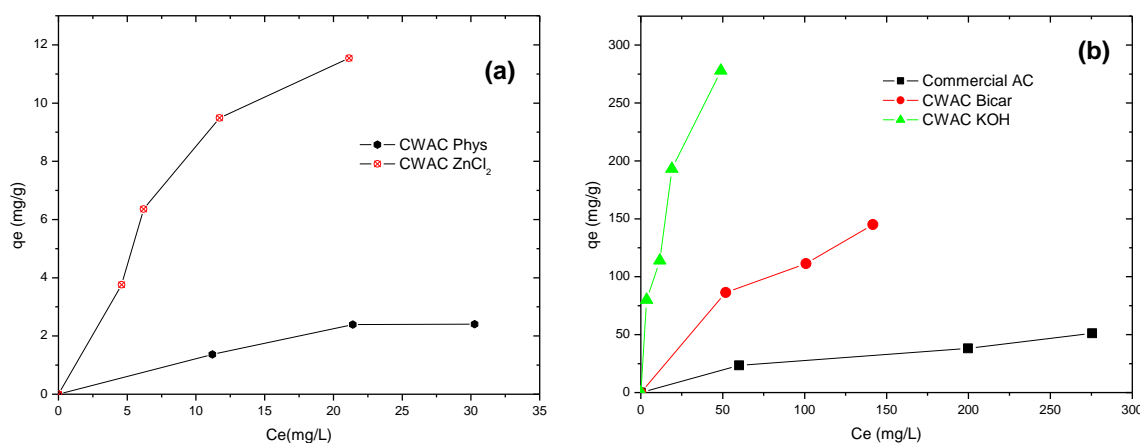


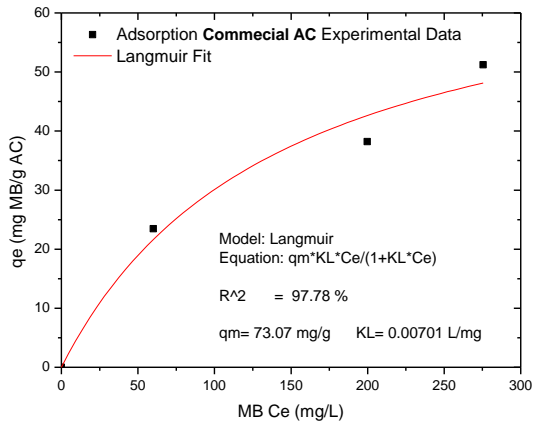
Figure. 3.3. MB adsorption isotherms (a) CWAC Phys and CWAC ZnCl₂ (b) Commercial AC, CWAC Bicar and CWAC KOH.

MB adsorption Experimental isotherms data were fitted with the Langmuir model (Eq.2.5) using the Origin.7 software. The figure 3.4 shows the fitting curves and confirm that all isotherms obey to Langmuir model.

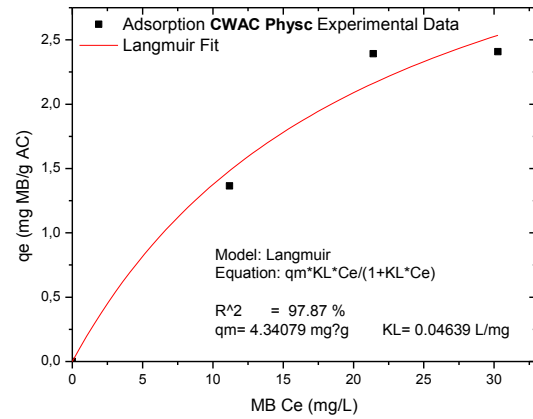
The values of the Langmuir parameters q_{max} , K_L and the correlation coefficient are listed in the table 3.6. These values, as expected confirm the SBET results (figure.3.5). Indeed, CWAC KOH has the highest MB adsorption capacity while, CWAC adsorbs the lowest amount of MB.

Table.3.6 Langmuir parameters q_{max} , K_L and the correlation coefficient.

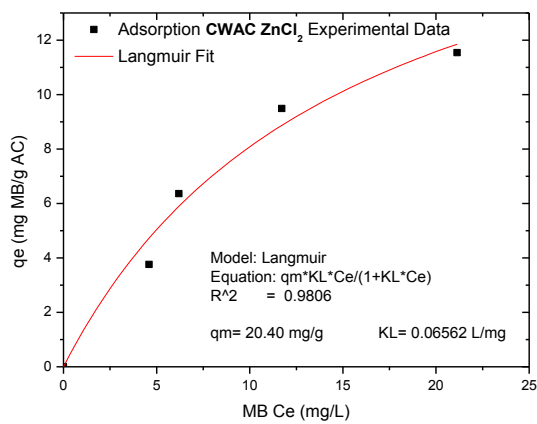
Activated Carbon	MB Maximum adsorbed amount q_{max} (mg/g)	Langmuir K_L (10^{-3} L/mg)	R^2 (%)
CWAC ZnCl ₂	20.40	65.62	98.1
CWAC KOH	404.54	44.43	97.3
CWAC Bicar	237.92	10.12	98.9
CWAC Phys	4.30	46.39	97.9
Commercial AC	73.07	7.01	97.8



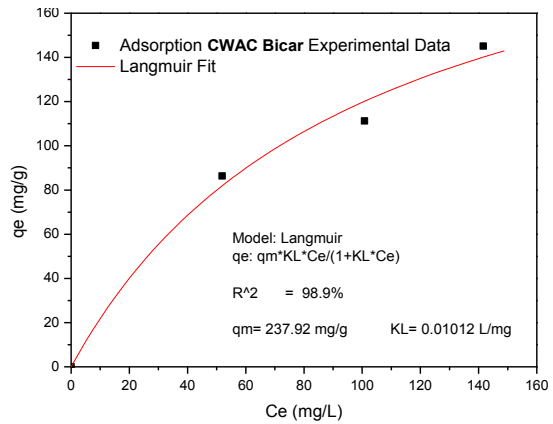
(a)



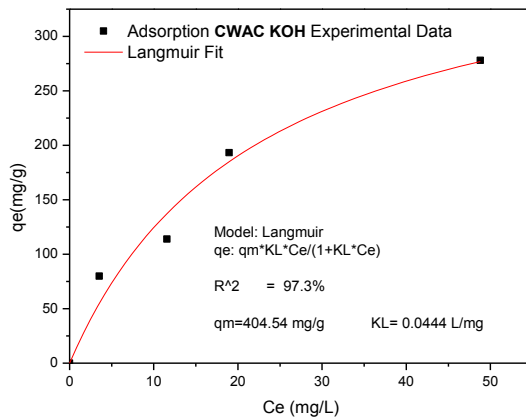
(b)



(c)



(d)



(e)

Figure. 3. 4. MB adsorption isotherms fitting with Langmuir model: (a) Commercial AC, (b) CWAC Physc, (c) CWAC ZnCl₂, (d) CWAC Bica and (e) CWAC KOH.

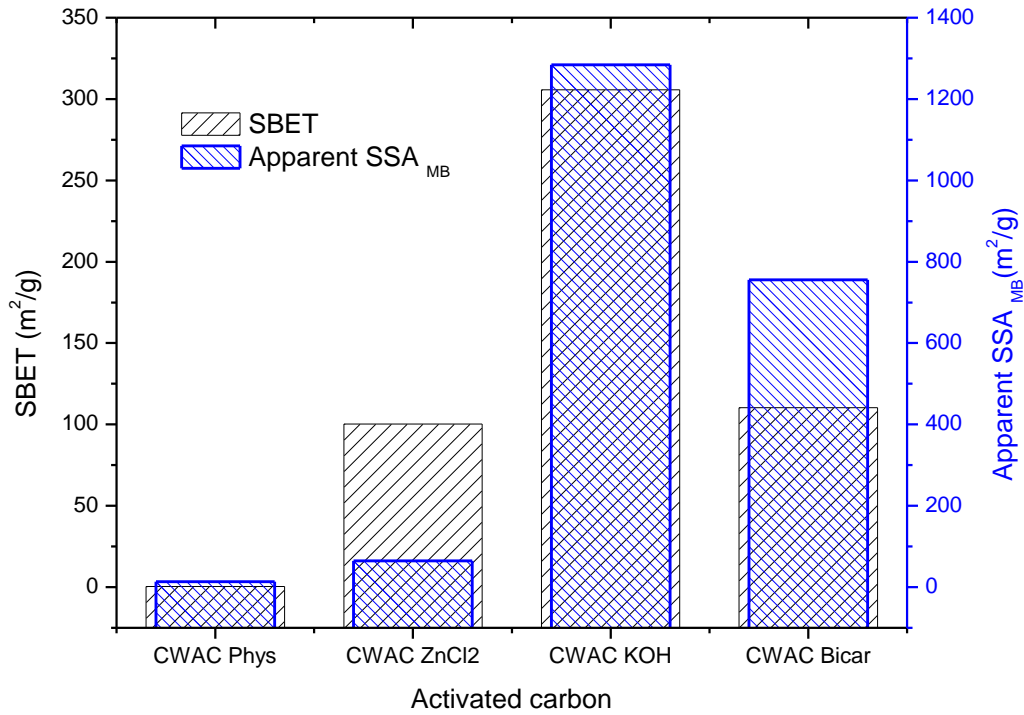


Figure 3.5. Correlation between BET specific surface area and apparent specific surface area determined by MB adsorption in liquid phase.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L defined by:

$$R_L = 1 / (1 + K_L \times C_0) \quad \text{Eq.3.1}$$

where

K_L is the Langmuir constant (L/mg) and

C_0 is the initial dye concentration (mg/L),

R_L value indicates the nature adsorption to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$ (28).

The figure.3.6 shows the evolution of R_L for all prepared activated carbons. All the R_L values are greater than 0 but less than 1 indicating that Langmuir isotherms are favorable for all prepared activated carbons. However on can observe two domains in the initial concentration: From 0 to 40 mg/L corresponding to CWAC Phys with the highest values of R_L showing that this activated carbon is not efficient and limited for the diluted solutions of pollutant. The second domain shows that the other activated are efficient for larger domain of application in term of initial concentration .

R_L values indicate the type of isotherm. An R_L value between 0 and 1 indicates favorable adsorption [29]. The R_L values were found to be between 0 and 1 for dye concentrations of 20, 40, 60 and 80 mg/L.

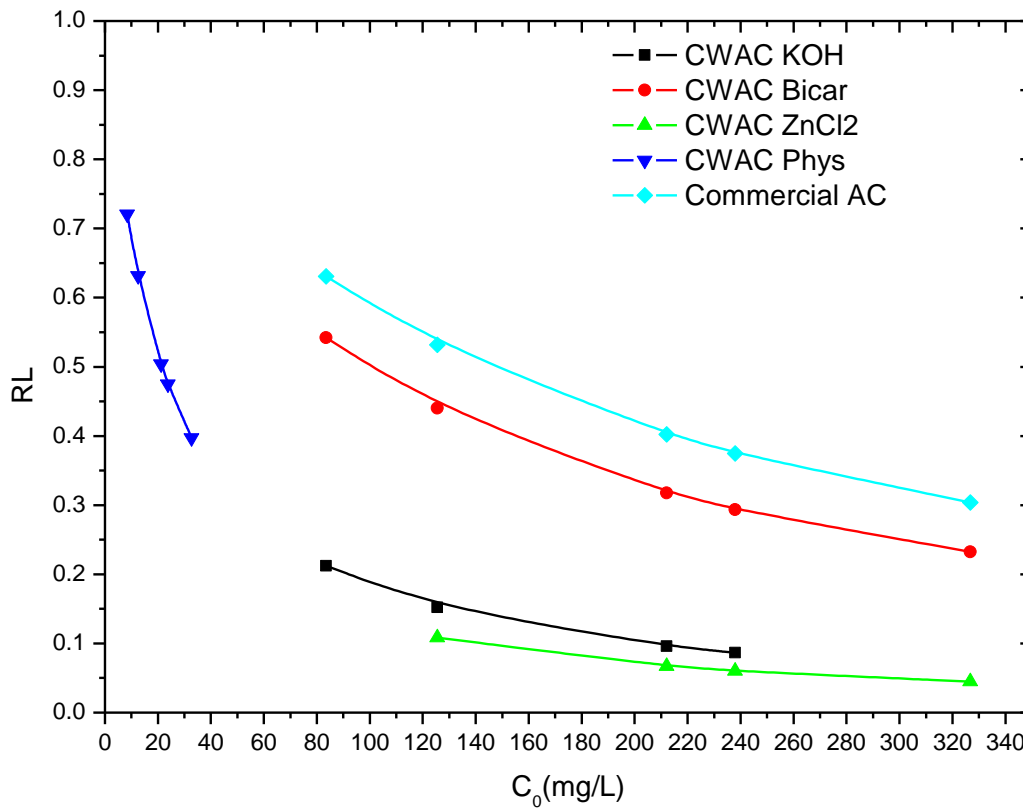


Figure.3.6. Evolution of R_L with initial concentration for all prepared activated carbons.

3.3. Infrared analysis (FTIR):

The study-infrared spectroscopy (transmission) of the coffee waste biomass is carried out on an FTIR spectrometer (type) at room temperature (wave number between 450 and 4000 cm^{-1}) The figure.3.7 shows the IR spectrums obtained for the coffee waste raw material and the CWAC KOH prepared activated carbon. Band assignments for Fig. 3.7 are summarized in Table 3.7.

The FTIR spectrums show characteristics band of lignocellulosic materials. A strong broad O-H band in $\sim 3400 \text{ cm}^{-1}$; a band in $\sim 2900 \text{ cm}^{-1}$, referent to a C-H stretching vibrating in methylene group; a band in $\sim 1650 \text{ cm}^{-1}$, referent to a C=O stretching vibrating in ketone, a band in $\sim 1500 \text{ cm}^{-1}$, referent to a C=C stretching vibrating in aromatics and a band in ~ 1000 to 1200 cm^{-1} referent to a C-O of cellulose, hemicelluloses and lignin. One can also distinguish the presence of C-N stretching vibrating. Similar data have been obtained by

Boonanmnuayvitaya, Chaiya et al, and Boonanmnuayvitaya, Sae-ung et al, for activated carbon from coffee residues.(30) (31).

In the CWAC KOH spectrum, the band in $\sim 3400\text{ cm}^{-1}$ (refers to O-H hydrophilic group) is still observed (but notably less intense). On the other hand, the bands in $\sim 2900\text{-}2800\text{ cm}^{-1}$ (C-H hydrophobic group) appears only in the raw coffee waste spectrum. The band in $\sim 1750\text{-}1650\text{ cm}^{-1}$ (C=O hydrophilic group) is more intense in CWAC KOH spectra. CWAC KOH activated carbon seems to have more hydrophilic groups than CW raw material. Finally, the carbonization of the material effect can be observed in the fact that the band in $\sim 2900\text{-}2800\text{ cm}^{-1}$ almost disappears. It should be notice a band in $\sim 1000\text{ cm}^{-1}$, present in the CW raw material spectrum and not present in the other spectra. This band can suggests the presence of a C-N bond, since the amount of nitrogen in CW raw material is three times higher than the amount in CWAC KOH (32).

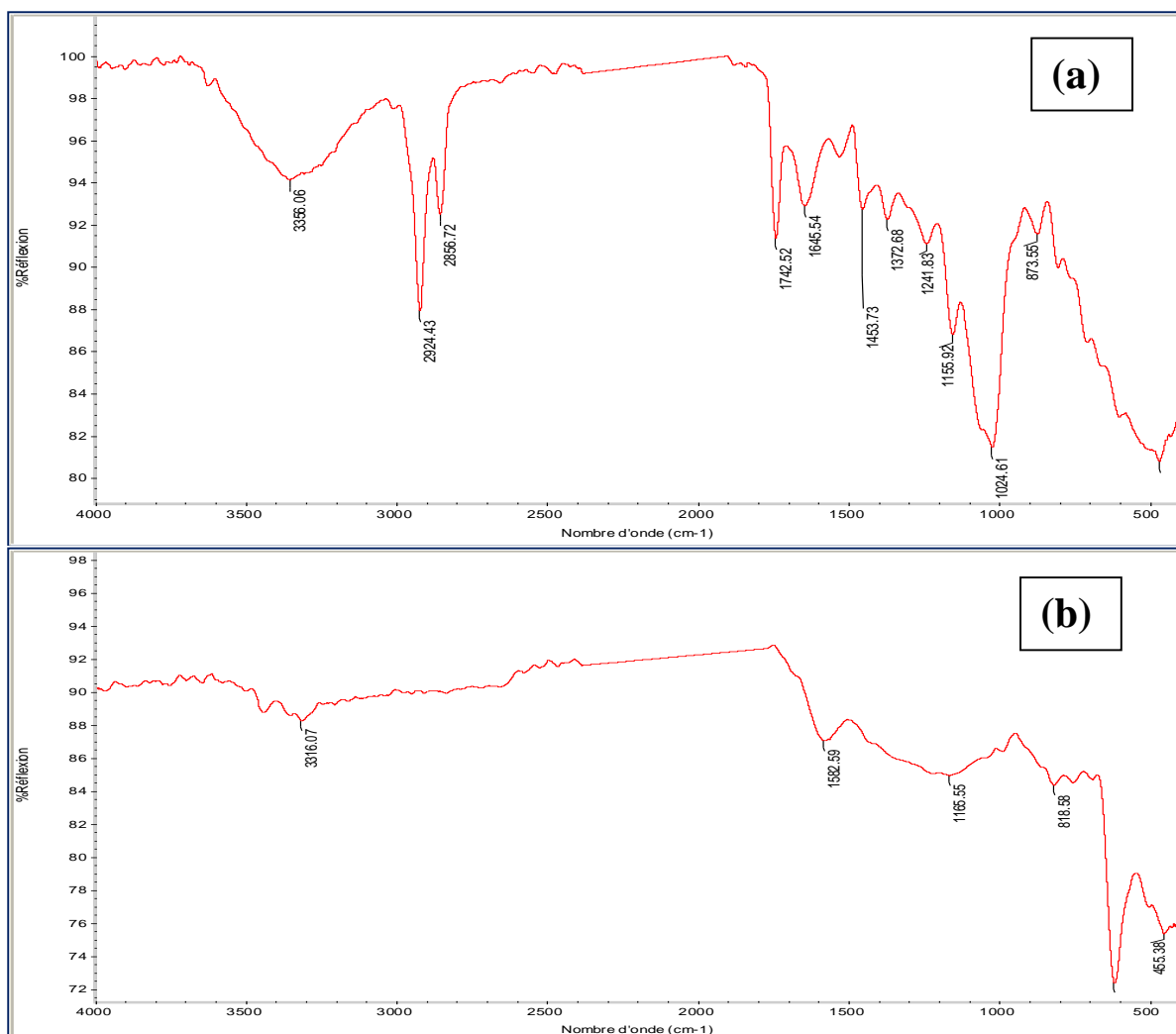


Figure.3.7 . FTIR spectrums of (a) Coffee waste raw material and (b) CWAC KOH.

Table.3.7. IR bands observed in the FTIR spectra of biomass.

Band number (cm ⁻¹)	Assignment
3594	O - H stretching vibration in free O H
3333, 3320	O- H stretching vibration in hydrogen bonds
3212	O -H stretching vibration in phenol
2834, 2882, 2884, 2974, 2981	C -H stretching vibration in methyl group
2823, 2886, 2889	C- H stretching vibration in methylene group
2756	C- H stretching vibration in aromatic
2699	C- H stretching vibration in aldehyde
2132, 2174	C≡C stretching vibration in alkyne
1612, 1631, 1656, 1657, 1695, 1732	C=O stretching vibration in ketone
1559, 1570, 1585	C=C stretching vibration in aromatic
1467	C -H deformation vibration in methylene group
1439	C- H deformation vibration in -C(CH ₃) ₃
1418	C -H deformation vibration in alkane
1161, 1206, 1218	C- O stretching vibration in alcohol

Conclusion:

The coffee waste activated carbons (CWAC) were prepared by the chemical activation with KOH, ZnCl₂ or NaHCO₃ followed a single step carbonization under the same conditions (argon atmosphere at 750 °C during 1h). These activated carbons were characterized by physical characterization, nitrogen adsorption–desorption isotherm, methylene blue adsorption and FTIR. The activated carbon prepared by KOH impregnation and argon activation at 750 °C during 1h , CWAC KOH, exhibited the highest adsorption capacity owing to the hydrophilic functional groups of O- H, C=O, C- O detected on the surface. CWAC KOH yields also, the highest total surface area (305.62 m²/g) and total pore volume (0.162 cm³/g) and the highest efficiency vis-a-vis the MB adsorption (404.54mg/g) and a notably important apparent specific surface area (1284.43 m²/g). Therefore the surface chemistry of activated carbon affects the adsorption capacity significantly while the texture characteristics of surface area and pore volume play a minor role in methylene blue adsorption in liquid phase.

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Appendix:

Summary Report

CWAC KOH

Surface Area :

Single point surface area at P/Po = 0.200491524:	310.4030 m ² /g
BET Surface Area:	305.6224 m ² /g
Langmuir Surface Area:	395.8978 m ² /g
t-Plot Micropore Area:	262.7405 m ² /g
t-Plot External Surface Area:	42.8819 m ² /g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	23.738 m ² /g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	15.7401 m ² /g

Pore Volume :

Single point adsorption total pore volume of pores less than 1297.564 Å diameter at P/Po = 0.984853837:	0.162682 cm ³ /g
Single point desorption total pore volume of pores less than 936.258 Å diameter at P/Po = 0.978875291:	0.168398 cm ³ /g
t-Plot micropore volume:	0.119144 cm ³ /g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.052436 cm ³ /g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.040136 cm ³ /g

Pore Size :

Adsorption average pore width (4V/A by BET):	21.2919 Å
Desorption average pore width (4V/A by BET):	22.0400 Å
BJH Adsorption average pore diameter (4V/A):	88.355 Å
BJH Desorption average pore diameter (4V/A):	101.996 Å

Summary Report

CWAC ZnCl₂

Surface Area :

Single point surface area at P/Po = 0.200313304:	101.4803 m ² /g
BET Surface Area:	100.2948 m ² /g
Langmuir Surface Area:	131.1147 m ² /g
t-Plot Micropore Area:	76.4186 m ² /g
t-Plot External Surface Area:	23.8761 m ² /g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	13.635 m ² /g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	7.8118 m ² /g

Pore Volume :

Single point adsorption total pore volume of pores less than 1255.806 Å diameter at P/Po = 0.984340967:	0.059446 cm ³ /g
Single point desorption total pore volume of pores less than 828.419 Å diameter at P/Po = 0.976061989:	0.060930 cm ³ /g
t-Plot micropore volume:	0.034619 cm ³ /g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.034100 cm ³ /g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.028131 cm ³ /g

Pore Size :

Adsorption average pore width (4V/A by BET):	23.7086 Å
Desorption average pore width (4V/A by BET):	24.3002 Å
BJH Adsorption average pore diameter (4V/A):	100.037 Å
BJH Desorption average pore diameter (4V/A):	144.044 Å

Summary Report

CWAC Bicar

Surface Area :

Single point surface area at P/Po = 0.200404292:	111.8374 m ² /g
BET Surface Area:	110.3862 m ² /g
Langmuir Surface Area:	143.6246 m ² /g
t-Plot Micropore Area:	88.3550 m ² /g
t-Plot External Surface Area:	22.0313 m ² /g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	10.319 m ² /g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter:	0.7621 m ² /g

Pore Volume :

Single point adsorption total pore volume of pores less than 1264.957 Å diameter at P/Po = 0.984456304:	0.061319 cm ³ /g
Single point desorption total pore volume of pores less than 722.861 Å diameter at P/Po = 0.972480134:	0.062127 cm ³ /g
t-Plot micropore volume:	0.040107 cm ³ /g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.021799 cm ³ /g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.009070 cm ³ /g

Pore Size :

Adsorption average pore width (4V/A by BET):	22.2198 Å
Desorption average pore width (4V/A by BET):	22.5126 Å
BJH Adsorption average pore diameter (4V/A):	84.499 Å
BJH Desorption average pore diameter (4V/A):	476.038 Å

Summary Report

CWAC Phys

Surface Area :

Single point surface area at $P/P_o = 0.034706027$: 0.4631 m²/g

Pore Volume :

Single point adsorption total pore volume of pores
less than 7584.902 Å diameter at $P/P_o = 0.997460684$: 0.007623 cm³/g

Pore Size :

Adsorption average pore width (4V/A by single point): 658.3636 Å