An-Najah National University

Faculty of Graduate Studies

Activated carbon from Cyclamen Persicum Tubers for Diclofenac removal from aqueous solution

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Dedication

To my father Spirit ,to my beloved mother, who raised me to be I am today... ….

To my brothers , my sister and their families who have supported me …..

To the memory of my dearest friends …….

I dedicate this work

Acknowledgement

First of all, I would like to express my gratitude to ALLAH s.w.t. for helping me to complete my study.

Many thanks and gratitude to my supervisors; Dr. Shehdeh Jodeh and Dr.Nidal Jaradat for their academic, technical guidance and full support during thesis work.

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My deepest gratitude to my family; who enlightened my academic path with care and support.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان :

Activated carbon from Cyclamen Persicum Tubers for Diclofenac removal from aqueous solution

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي لخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى .

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student Name: **إسم الطالب:**

Signature: **التوقيع:**

Date: **التاريخ:**

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List of Abbreviation

C_e : Equilibrium concentration of the adsorbate.

C_i : Initial solution concentration.

$\mathbf{K_L}$: Langmuir constant.

K_F Freundlich relative adsorption capacity constant.

q_t **:** Adsorption capacity at time *t.*

k_1: Pseudo-first-order rate constant.

$\mathbf{k_2}$**:** Pseudo second order rate constant.

K`: Equilibrium constant of adsorption.

C_o : Initial solute concentration fed to fixed bed.

$\mathbf{C_t}$: adsorbate concentration in the fluid phase at time t.

Abs: Absorbance.

AC: Activated carbon.

CTAC : Cyclamen tubers activated carbon.

IN : iodine number (mg/g).

K* : Equilibrium rate constant of second-order kinetic model.

PR : percentage removal (%).

$\mathbf{q_e}$: Amount of adsorbate per unit mass of adsorbent at equilibrium(min).

$\mathbf{q_t}$: Amount of adsorbate per unit mass of adsorbent at time t (min).

DCF: Diclofenac sodium.

R : Correlation coefficient.

$\mathbf{V_b}$: are volumes of sodium thiosulfate solution required for blank .

$\mathbf{C_v}$: cylinder volume packed with dried activated carbon (ml).

$\mathbf{V_s}$: are volumes of sodium thiosulfate solution required for sample titrations(mL) .

ΔH° : standard enthalpy of a reaction.

ΔS° : standard entropy of a reaction.

ΔG°: standard free energy .

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Abstract

The aim of this work was to evaluate the antibacterial activity of the crude methanolic extract obtaining from cyclamen persicum tubers and to re-use the remaining tissues after extraction process to prepare activated carbon by different methods then to set up a thermodynamic and kinetic study of diclofenac sodium (DCF) pharmaceutical adsorption from aqueous solution onto this activated carbon from cyclamen persicum tubers.

The prepared activated carbon samples were compared using Surface area determined by iodine number method, scanning electron microphages (SEM) and FTIR analysis. DCF adsorption onto activated carbon was studied by batch experiments. The adsorptive properties of cyclamen tubers activated carbon (CTAC) was investigated and compared with Eucarbon® ; the available charcoal in the market, DCF concentration, pH, temperature and contact time parameters were studied .

To investigate the nature of the surface and adsorption capacity of CTAC, Freundlich and Langmuir models were used to study adsorption isotherm at equilibrium. In order to determine whether the adsorption process is chemical or physical, three kinetics models were used. Thermodynamic

study was carried out to determine if adsorption of DCF onto CTAC was exothermic or endothermic reaction.

Results indicated antibacterial activity of the crude methanolic extract against *staphylococcus. aureis* gram positive bacterial strain; using (MHA) plate that showed zone of inhibition after overnight incubation at 37 °C, the yield of this extract was 9%(w/w).

Results also showed that the activated carbon produced from cyclamen tubers gives highest percentage yield which reaches up to 51.8%, using phosphoric acid as activating agent, while largest Surface area determined by iodine number was 606.78 mg/g using zinc chloride as activating agent, SEM analysis showed that KOH produced the most porous structure in CTAC.

Optimum percent of DCF removal was 72% when CTAC dosage was 0.25g and DCF concentration 50mg/L. Percentage removal of DCF increases when the concentration of DCF increases as the maximum percentage removal reached 81% when DCF concentration was 70mg/L and 0.7g CTAC and pH ranging from 6 to 2.

The effect of temperature on adsorption by CTAC and Eucarbon® has also been investigated in the range of 15-45 °C. The results indicated that the temperature significantly affected DCF adsorption on both adsorbents.

The equilibrium time for DCF adsorption was 120 min for CTAC and 150 min for Eucarbon®, but most of the adsorption attained within the first 15 min using CTAC while 30 min was needed for Eucarbon®.

Frenundlich model describe adsorption isotherm of DCF more efficiently onto CTAC with n equal to 1.398 that indicated favorable adsorption. This finding validated the assumption of multilayer physical adsorption process of DCF. Pseudo-second order reaction model is the best for describing adsorption of DCF with correlation coefficient closes to unity, this validated that the adsorption process was physical one, adsorption process was exothermic as $\Delta S°$ had negative charge, and also as $\Delta H°$ was less than 40 Kj / mol lthis suggesting a physisorption process. Concerning the change in free energy, the adsorption process of the DCF onto CTAC was spontaneous, depending on temperature.

Chapter 1

General Introduction

1.1. Research overview

Recently, carbon has been one of the magnificent elements which have revolutionized material science. From carbon we obtain the best porous adsorber (activated carbon) with excellent properties for large spectrum of industrial and medicinal applications, the use of activated carbon in medicine has a long historical tradition. Even the ancient Egyptians knew about the medical use of charcoal 1550 years before Christ. At the end of the 18th century, the German chemist Carl Wilhelm Scheele observed the adsorption capacity of coal for gases [1].

Due to their fine distribution and large surface activated carbon is largely capable of binding other substances, by this the harmful agents lose their capability to affect the human body. The medical activated carbon is obtained by the carbonization of raw materials at high temperatures: Vegetable raw materials, such as wood, peat, walnut shells or coffee beans can be used. Together with dehydrating agents they are heated up from 500 to 900 ºC and subsequently cleaned by a washout, to obtain an activated carbon using chemical activator agent [2].

Carbenous material can be also activated by controlled pyrolysis of coconut shells, bone, peat, lignite (coal), wood or petroleum under the flow of steam, nitrogen gas or carbon dioxide at high temperatures (600-900 ºC). It

is washed with organic acids and dried. This “activation” creates the highly developed internal pore structure and small particle size needed for effective gastrointestinal decontamination. This “activation” also removes substances previously adsorbed by the charcoal. For optimal adsorption, charcoal should have small particle size, a large total surface area, and a low mineral content. Optimal activated charcoal should have a surface area of up to 1,000 m^2/gram [3].

The amount of drug that adsorbs to the activated charcoal is dependent on the charcoal-to-drug ratio, with the optimal ratio proposed to be 10:1.7 As the dose of drug is rarely known, a standard dose of charcoal is normally given. Toxin adsorption may be pH dependent, as these substances are more likely to bind to activated charcoal in the unionized state. Higher doses may be needed in the presence of food [4].

Activated charcoal has been shown to be effective agent in treatment of drug poisoning cases due to its ability for drug adsorption, and then reduces drug absorption into blood stream. A number of studies have investigated the effects of activated charcoal on acetaminophen poisoning. The first study compared three different decontamination methods in patients ingesting 5g or more acetaminophen and showed that single dose AC decreased the absorption of acetaminophen [5].

On the other hand many drugs and chemicals known to have little effect from the administration of activated charcoal include common electrolytes, iron, mineral acids or bases, alcohols, cyanide, most solvents, water

insoluble compounds such as hydrocarbons, lithium and other heavy metals, this confirmed the suggested idea in using AC as antidote in drug poisoning cases [6].

Activated charcoal is also an effective remedy that can be used in a lot of different conditions, such as :

Diarrhea ; by taking powdered activated charcoal along with clear liquids such as vegetable broths, herbal teas (red raspberry, chamomile, and peppermint), will reduce electrolytes loss and to prevent dehydration which caused in this condition. *Food Poisoning*; charcoal is very effective for food poisoning as taking 1 tablespoon of charcoal in a glass of water then drinking another glass of water will relieve food poisoning symptoms especially diarrhea and abdominal pain. *Gases* (Flatulence); activated charcoal will absorb gases very quickly and give relief of flatulence and finally activated charcoal will be agood choise in *indigestion* by taking 1 - 2 tablespoonful of activated charcoal stirred in a glass of water will facilitate digestion , and relieve the symptoms of gastric upset [7].

Commercial activated carbon is commonly produced from naturally occurring carbonaceous materials such as coal, wood and peat, bones, agricultural by products ,dried sewage sludge, carbonaceous materials also can be obtained from paper mill sludge, old newspapers and waste tires[8].

On the other hand developing activated carbon for medicinal purposes focuses on herbal resources as precursors of the carbonaceous material such as vegetable residues, coconut-shell, palm seeds, olive stones, mixture of apricot and peach stones, rice husks etc…[9].

1.2. Hypothesis of this work

This research is based on the hypothesis that Cyclamen Persicum tubers will form an efficient source for developing herbal activated carbon with high capacity for adsorption of various toxic materials as these tubers were observed to retain and absorb water in high capacity for long time as it is grown at rocky areas .

Also in this research a crude methanolic extract from cyclamen tubers will be tested on *staphlococcus. aureus* bacterial strain in order to develop an active ingredient for food poisoning treatment caused by this type of microbes .

1.3. Objectives

The following objectives serve the goal of this research, which are:

- Isolation of crude methanolic extract from cyclamen tubers and investigation of its anti bacterial activity.
- Production and characterization of activated carbon from the remained tissues after the extraction process from cyclamen tubers.

- Study the effect of chemical activation on the development of pore structure of the produced activated carbon.
- Study adsorption isotherms, kinetics and thermodynamics of diclofenac sodium pharmaceutical adsorption onto activated carbon produced from these tubers.
- Compare the adsorption capacity of this prepared activated carbon with Eucarbon®; the available medical charcoal in the market.
- Developing an alternative drug for food poisoning treatment by incorporating the extracted active ingredients with the prepared activated carbon from these tubers.

1.4. Methodology

This project methodology is focused on making cyclamen persicum tubers a good commercial source for medical applications, this is will be achieved by the following two reaserches on these tubers.

In this research, obtaining a crude methanolic extract from cyclamen persicum tubers was carried out by simple refluxing method using methanol as a solvent for extraction, this extract was tested on staphylococcus. aureus bacterial strain which causes usually food poisoning.

The remaining cyclamen tubers tissues after extraction process were kept to be used for the production of activated carbon by different method.

In this research, the production of activated carbon was carried out by using

chemical impregnation and physical activation. In physical activation, the carbonization and activation were accomplished in a single step by carrying out the thermal decomposition of the raw material under nitrogen gas flow.

While chemical impregnation with certain activating agents was carried out in chemical activation process before carbonization. Three activating agents were used, phosphoric acid, zinc chloride and potassium hydroxide. Zinc chloride acts as a Lewis acid which is a strong dehydrating agent that could modify the structure of carbon to form the porous structure. While phosphoric acid, was also known as a strong acid acts as an acid catalyst to promote cleavage reactions [10].

Potassium hydroxide is a strong base that react with the precursor by exothermic reaction that leads to the formation of functional group –OK. This bond oxidizes and removes the cross linkage between adjacent graphene layers [11].

By using these three chemicals, the influences on the pore structure of the produced AC can be accomplished, after the impregnation step, the samples were carbonized in the horizontal furnace without using nitrogen gas as inert atmosphere.

Chapter 2
Crude methanolic extract with antibacterial activity from Cyclamen Persicum tubers

2.1. General background

Cyclamen plant is a genus of 20 species of perennials belonging to Primulaceae family growing from tubers valued for their flowers, leaves and tubers. Cyclamen species are native to Europe, Turkey and the Mediterranean countries [12]. In figure 2.1 cyclamen plant consists mainly of four parts:

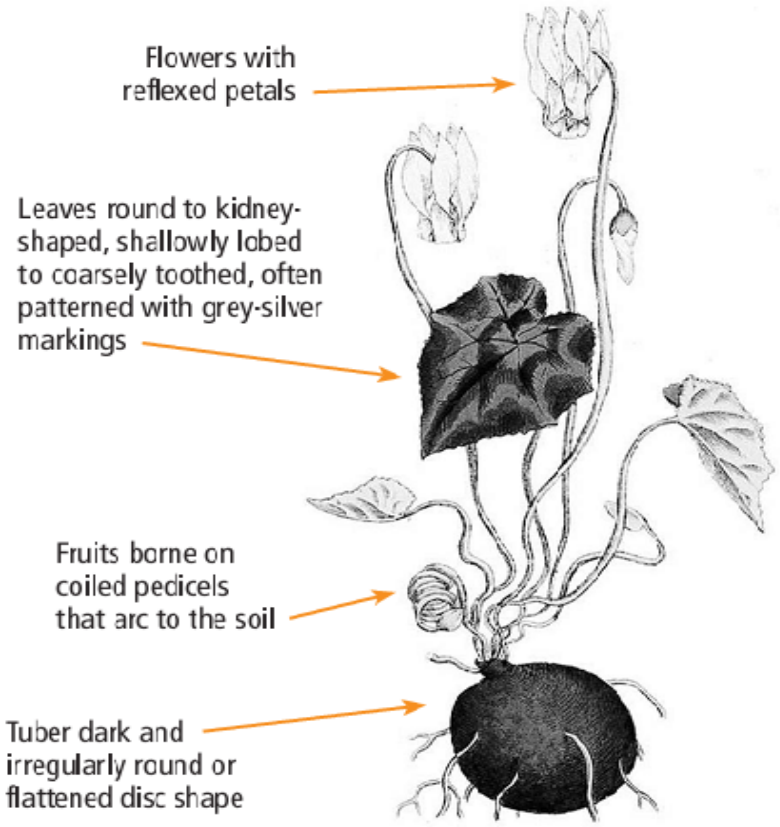


Figure (2.1) : Cyclamen persicum plant parts

The word "cyclamen" comes through Latin from the Greek cyclamīnos meaning "circle", with reference to the shape of the tuber [13].

Tubers of cyclamen species are the storage organs from which flowers and roots grow. It is a round in shape and develops from the hypocotyl (the stem of a seedling). It is often mistakenly called a corm, but a corm (found in crocuses for example) is defined as having a papery tunic and a basal plate from which the roots grow. The storage organ of the cyclamen has no papery covering and, depending on the species, roots may grow out of any part [14].

The tuber may produce roots from the top, sides, or bottom, depending on the species. Cyclamen persicum and Cyclamen coum root from the bottom; Cyclamen hederifolium roots from the top and sides. Cyclamen graecum has thick anchor roots on the bottom. The shape may be near spherical, as in Cyclamen coum or flattened, as in Cyclamen hederifolium. In older specimens of Cyclamen purpurascens and Cyclamen rohlfsianum, growing points on the tuber may become separated by shoulders of tissue, In most other species, the tuber is round in old age.

Leaves and flowers sprout in rosettes from growing points on the top of the tuber. Growing points that have lengthened and become like woody stems are known as floral trunks.

The size of the tuber varies depending on species. In Cyclamen hederifolium, older tubers commonly reach 24 cm (9.4 in) across, but in Cyclamen parviflorum, tubers do not grow larger than 2 cm (1 in) [15] .

2.1.1. Cyclamen persicum tubers in folk medicine

Several species of cyclamen plant tubers are widely used in traditional folk medicine for their laxative and abortive effects, and anti-helmintic properties [16].

In Turkish folk medicine tubers of Cyclamen are used as an ovule in their natural form after removal of the outer surface, against infertility [17].

Pharmacological investigations on the methanolic extracts of Cyclamen spp. tubers exhibited in the vitro cytotoxic activity [18]. Also spermicidal effects of the cyclamen tubers extracts approved in some reaserches in 1985 [19].

In Europe the extract of cyclamen tubers was used as antimicrobial agent due to its potency showed in vitro against bacteria [20].

Cyclamen tubers were used also for dermatological purposes due to their anti inflammatory effects [21].

Also Fresh tubers of C. hederifolium were used in some parts of Itally to treat hemorrhoids [22] .

2.1.2. Recent reaserches on cyclamen tubers

Antimicrobial activity tests were carried out against the bacteria Pseudomonas aeruginosa , Salmonella choleraesuis . these tests show inhibitory effects of cyclamen extracts against thses bacterial strains [23].

Analgesic and anti-inflammatory activities was investigated at cyclamen repandum tubers [24].

Early investigations on the different Cyclamen species resulted in the isolation of triterpenoid saponins [25] .

A piperidine alkaloid and sterols were isolated from cyclamen coum tubers [26].

The anthocyanin and flavonoid pigments of many Cyclamen cultivars have also been investigated by various groups to show their effects in pigmentation [27].

As a part of our ongoing studies on bioactive triterpenoid sapo-nins, we investigated the chemical constituents of C. hederifolium.

Researches now adays are carried on Cyclamen tubes in order to isolate active ingredients pocessing therapeutic effects on human.

Triterpene glycoside, repandoside was isolated from the methanol extract of Cyclamen repandum tubers. The isolated saponin was characterized by high resolution mass spectrometry and both 1D and 2D NMR

experiments.Antiinflammatory effect of this isolated saponin was investigated in vitro to acheive good effects [28].

The structure of isolated saponin is given in figure (2.2)

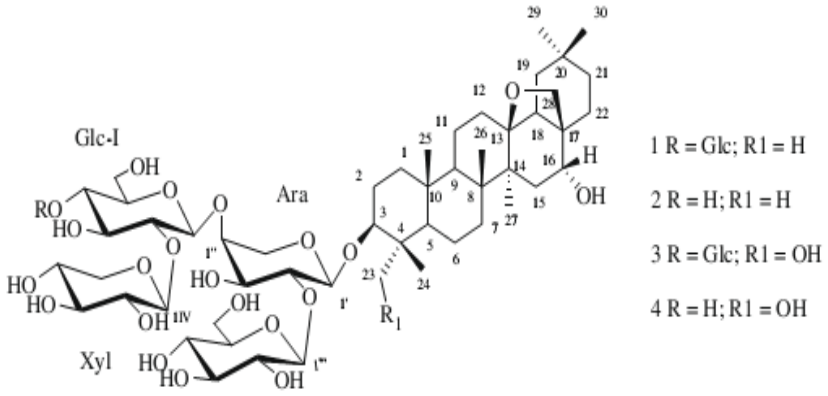


Figure 2.2 : saponin glycoside structure from Cyclamen repandum tubers

Further investigation on this triterpene glycoside was carried out, to test the anti proliferative activity in different cancer cell lines including Hela (human cervical cancer cells), H-446 (human lung cancer cells), HT-29 (human colon carcinoma cells), U937 (human leukemia cells). In a range of concentrations between 1 and 50 M, none of the tested compounds caused a significant reduction of the cell number as compared to control [29].

In this research anti bacterial activity of methanol extract was investigated against *S. aurous* bacterial strain in order to develop a new alternative drug for food poisoning cases.

2.1.3. Staphylococcus aureus bacteria

It is a facultative anaerobic, Gram-positive coccus, it has a golden color on the agar plate, aureus means "golden" in Latin.

S. aureus was discovered in Aberdeen; Scotland in 1880 by the surgeon Sir Alexander Ogston in pus from surgical abscesses [30].

S. aureus can cause a range of illnesses like minor skin infections, food poisoning, life-threatening diseases such as pneumonia, meningitis, osteomyelitis, endocarditis, toxic shock syndrome (TSS), bacteremia and sepsis [31].

As pathogenic bCFacteria in the human food chain staphylococci are one of the most predominant bacterial species encountered during poultry slaughter and processing. They have been recovered from air samples , neck skin of chicken carcasses, equipments and machinery surfaces.The foods that most frequently cause Staphylococcus aureus food poisoning are red meat, poultry and their products [32].

2.1.4. Saponin as an antibiotic alternative

- **Characteristics of Saponins**

Saponins acquired their name from the soapwort plant (Saponaria root) which was used as soap. Saponins are generally identified by their bitter taste, throat irritation, froth and foam formation in aqueous solutions, fish toxicity, and ability to lyse erythrosites [33].

Some saponins even have been used as flavor enhancers and sweeteners in foods and cigarettes. For example, the flavor enhancer, licorice root extract is rich in the saponin glycyrrhizin, and saponins from the roots of

Glycyrrhiza glabra are 941-fold as sweet as sucrose and 60 times sweeter than cane sugar [34].

- **Chemical Nature of Saponins**

Saponins are synthesized by a common metabolic pathway starting from acetyl co-enzyme A. Mevalonic acid and then squalene are the intermediary products for both triterpenoidal and steroidal saponins. In general, synthesis of cholesterol, other steroids, and saponins proceed through a common synthetic pathway[35].

Saponins are glycoside compounds whose chemical structures are composed of a fat-soluble nucleus called the aglycone part that is either triterpenoid (C-30), or neutral or alkaloid steroids (C-27) . One or more sugar side chains called glycones can be linked through ether and ester linkages to the aglycone nucleus at glycosylation sites. Triterpenoid saponins naturally occur as saponin or free aglycone forms, while steroid saponins occur only as saponins and never in the free aglycone form. The molecular weights of saponins range from 1000 to 1500 Daltons [36].

- **Antibacterial and biological Activities of saponin**

The antibacterial activity of saponins is affected by factors such as the aglycone part, number, position and chemical structure of sugar side chain.

Many saponins are antimicrobial and considered as a part of plants' defense systems. Plants known to have antimicrobial activity include

yucca, ginseng, and triterpenoid saponins from Holothuroidea class of marine echinoderm animals [37].

Not all saponins have antibacterial activity. For example, medicagenic and zanhic acid saponins isolated from alfalfa plants do not show activities against Escherichia coli, Staphylococcus aureus, Bacillus subtitles, Pseudomonas aeruginosa and Mycobacterium intracellular [38].

Antibacterial activities of saponins differ according to type of the bacteria. Some saponins such as ivy saponin, spirostanol saponin, asterosaponin from starfish, and yucca saponin show more antimicrobial activity against gram positive bacteria (Staphylococcus aureus) than gram-negative bacteria (Escherichia coli) at the same concentration. It was noted that saponin-rich yucca extracts in ruminant diets decreased cellulolytic bacteria while not affecting amylolytic bacteria [39].

Quillaja saponin (Quillaja saponaria) and yucca saponin (Yucca schidigera) obtained from different commercial companies exhibited antibacterial activity against Escherichia coli K-12 with different efficiencies, suggesting that saponins from various sources differ in their biological activity due to their different chemical structures and extraction procedure [40].

Extraction methods and fat content have important effects on the antibacterial activity of the resultant plant extracts. For example, fat free extracts from Bauhinia variegata L. bark were more active than high fat

extracts against gram-positive bacterial strains such as Staphylococcus aureus. However, fat free extracts exhibited either similar or less antibacterial activity than high fat extracts against gram-negative bacterial strains such as Escherichia coli.

Many of the biological activities mentioned above can be mediated by interaction of saponins with cell surface proteins and receptors, secondarily affecting enzymes.

Saponins also affect hormone activity. For example, saponins exhibit strong stimulation effects on both adrenocorticotropic hormone (ACTH) and corticosterone hormone . They show mineralocorticoid-like activity by transforming biologically active steroid cortisol hormone into its inactive metabolite, cortisone [41].

2.1.5. Toxicity of saponin

Many saponins exhibit toxic effects at high doses over long periods of time causing problems such as excessive salivation, vomiting, diarrhea, loss of appetite and manifestations of paralysis .Oral toxicity of saponins to warm-blooded animals is relatively low and LD50 (lethal dose, 50%) values are in the range 50-1000 mg/kg [42].

However, they are highly toxic when given intravenously. The toxic effects of many saponins are neutralized by saliva of animals such as sheep, intestinal bacteria [43].

Not all saponins are degraded at the same conditions and temperature. For example, oat saponins are not affected until heated to 140 °C for 3 h. Degradation increases as the pH decreases from 7 to 4 in avenacoside A. Saponin degradation sometimes induces activity of enzymes such as β-glycosidase that occur naturally in oat leaves. Removing the C-26-bound glucose moiety results in forming a monodesmosidic saponin with the highest antifungal activity [44].

Effect of Saponins on Intestinal Activity, nutrient Digestion and absorption showed that Saponins reduce intestinal motility , increase the transit time of ingesta, inhibit gastric emptying. Saponins can cause intestinal lesions, damage the intestinal villi and alter intestinal morphology in the lower intestine [45].

Many saponins decrease digestion by changing the site and the extent of nutrient digestion in ruminants and altering rumen fermentation. Total volatile fatty acid and microbial protein synthesis can be reduced. Digestive coefficients of some organic matterials such as hemicelluloses and cellulose are reduced and digestibility of some nutrients such as protein are also reduced perhaps potentianted by damage to the intestinal membranes[46].

2.2. Experimental set up

2.2.1 Materials and methodology

2.2.1.1 Plant material

Cyclamen persicum tubers were collected from different sites in Tulkarem and Nablus cities between the months of July and September, 2012. These tubers were identified by Dr. Nidal Jaradat, Faculty of pharmacy, An-Najah National University, Palestine. The tubers were sun dried, cut into small pieces then grounded using electronic grinder to obtain powdered tubers.

2.2.1.2 Crude methanolic extract from cyclamen tubers powder.

Simple refluxing method was followed for extraction of saponin glycosides from Cyclamen tubers powder by suspending (150 g) of this powder 400 ml methanol and refluxed with magnetic stirring for about 4 hours at 40ºC.

The refluxed extract was cooled then filtered and the resulting solution was evaporated to dryness to yield 19 g gummy yellow methanolic extracts which stored at room temperature until used in further studies.

The remained cyclamen tuber powder was washed thorouly by distilled water and dried at 110 ºC in an oven, to be used for activated carbon production .This crude extract was kept under 4 ºC temperature in air tight container.

2.2.1.3. Frothing test for saponin detection in this extract

Frothing test was acheived on the basis that aqueous solution of saponins form very stable foams, that lasts at least for 10 min.

So 1 ml of the concentrated methanolic solution of the extract was shaken with 5 ml of distilled water in a test tube. Formation of a stable foams for 10 min will indicate the presence of saponin glycosides.

2.2.1.4. Test for antibacterial activity

Sensitive microorganisms employed in this study Staphylococcus. aureus (Gram positive), was obtained from the Department of Microbiology and Parasitology- Faculty of Science; AL-Najah University.

Susceptibility test of ***s. aureus*** bacteria to the methanolic extrac was performed using surface of Muller-Hinton Agar (MHA) plates .Solution of this methanolic extrat has been prepared in concentration of 4 mg of extract per 1 ml of distilled water as a solvent .

This prepared solution was placed on the (MHA) plate containing bacteria and incubated for 24 h at 37 ºC. The sensitivity of s. aureus against saponin was evaluated by observing for zone of growth inhibition of this bacteria in the plate.

In Figure (2.3) staphylococcus .aureus bacterial colonies have been shown on (MHA) plate.

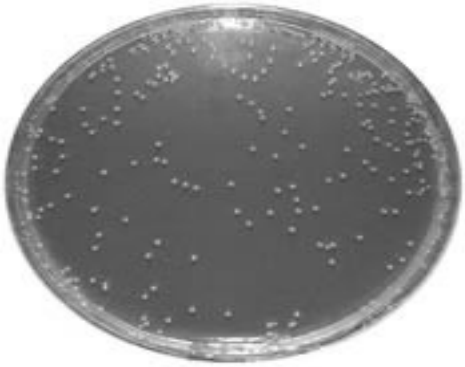


Figure 2.3 : *S. aureus* bacterial colonies on (MHA) plate

2.3. Results and discussion

The crude methanolic extract yield was calculated according to the following equation:

$$\text{Yield of the crude extract (wt \%)} = \frac{weight\ of \quad \text{extract}}{weight\ of\ \text{CT powder}} \times 100$$

This yield was 9% (w/w) of methanolic extract obtained from cyclamen persicum tubers.

Frothing test to indicate the presence of saponin glycosides in this extract showed positive result as one half cm foam lasted in the test tube for 10 min as shown in figure 2.4. So this extract forms a good source of saponin glycosides that can be further isolated.

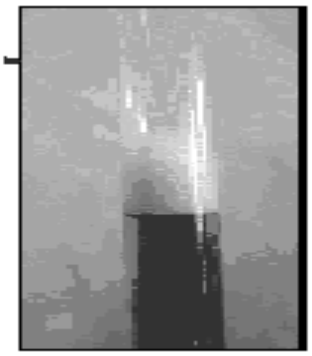


Figure 2.4 : frothing test for saponin glycoside detection

The yellow gummy extract exhibited in vitro anti bacterial activity against staphylococcus bacteria as inhibition zone of *staph .aureus* on agar plate (MHA) was observed after 24h incubation at 37ºC. this inhibition zone was measured in millimeter using transparent ruler at different dilution series as following:

Dilution factor	**inhibition zone (mm)**
Pure	11
1:1	9
1:4	-

These results indicated that methanolic extract from cyclamen tubers was active against gram positive staphylococcus aureas bacteria .

2.4. Conclusion

By this simple extract in method we concluded that a good yield of crude methanolic extract from cyclamen persicum plant tubers can be obtained , which exhibited in vitro antibacterial activity against gram positive staphylococcus .aureus bacterial strains.

Further investigations can be carried out on this extract for isolatinon of different types of saponin glycosides compounds in future works.

These compounds may have other antimicrobial activity against several types of microbes , this can be developed in more sophisticated researches.

Chapter 3
Activated carbon from Cyclamen Persicum Tubers for Diclofenac removal from aqueous solution

3.1. General background

Activated carbon (AC) is defined as a solid, porous, black, tasteless carbonaceous material, which have been subjected to reaction with gases during or after carbonization in order to increase porosity. AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface. The main features common to all AC are; graphite like referred to as Basic Structure other definition for AC is that it is an amorphous solid with a large internal surface area and pore volume [47].

For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater.The surface oxygen functional groups can be easily introduced to the carbon 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 ºC [48].

While wet oxidation methods involve the reaction between the carbon surface and solutions of oxidizing agents as phosphoric acid (H_3PO_4), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), zinc chloride ($ZnCl_2$), potassium

permanganate ($KMnO_4$), ammonium per sulphate $(NH_4)_2SO_8$, 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 [49].

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 by using phosphoric acid. However, phosphoric acid activation is widely preferred over zinc chloride because $ZnCl_2$ has bad environmental impact and the activated carbon produced when using it cannot be used in the food and pharmaceutical industries [50].

3.1.1. Activation methods for activated carbon production

Production of activated carbon involves the two main steps which are pyrolysis where the carboneous source materials are heated, decomposed and converted to carbonized material in the absent of air . Then, the process is continued by activation step which will increase the surface area of the carbonized material. At present, there are two different activation processes: (1) steam activation, (2) chemical activation. In steam activation, steam is introduced in temperature range 600-1200 ºC, whereas in chemical activation, raw material is impregnated with strong dehydrating

agent such as phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$) and then heat to 500-800 ºC to activate the carbon [51].

Activation process are discussed in detail as folowing:

- **Physical pyrolysis**

In physical pyrolysis method the raw material with less than 25% moisture, is carbonized first at 400 - 500 ºC to eliminate the bulk of the volatile matter and then the carbon is subjected to oxidizing gases usually carbon dioxide or steam at 800-1000 ºC or and with air at lower temperature, for selective oxidation. The oxidation is preceded usually by a primary carbonization of raw material. The pyrolysis of wood starts at temperature about 225 ºC .

Carbon is oxidized by atmospheric oxygen is exposed also to CO2, so the air should be excluded or very controlled during carbonizing and activating

The activation of charcoal consists in thermal treatment at high temperatures (800-1000 ºC), as a result, these incomplete combustion products burn up and volatilize [52].

- **Chemical activation**

Chemical activation has two important advantages when a lignocelluloses material is especially used as a raw material. One is the lower temperature at which the process is accomplished making the process more economical compared to physical activation. The other is that the yield of chemical

activation is relatively higher, since carbon burn-off char is not required The formation of tar and other by-products is inhibited by the chemical agent [53].

Examples of chemical activating agents used in this research include zinc chloride, phosphoric acid, or potassium hydroxide. The chemical is mixed with the precursor prior to a carbonization step. This carbonization is often milder in time and temperature than physical activation techniques. The chemical agent acts to restrict the formation of tar during the heat treatment within the carbon matrix. The chemical is then washed from the carbon, and a porous structure remains. Chemical activation often creates impressive pore structures with large surface areas, however the chemical addition and washing steps leave the resulting carbon with an acidic surface. This higher surface acidity can be deleterious to performance in some adsorption conditions [54].

3.1.2. Activated carbon efficiency

Activated carbon efficiency for removing a given substance depends on both its surface chemistry and its adsorption capacity. The AC adsorption capacity is usually attributed to its internal pore volume that may be distributed throughout the solid as pores ranging in width from micropores to macrospores. When the pore sizes of the activated carbon are in the size range of the pollutants, adsorption process will be enhanced and is expected to be efficient. Adsorption capacity of the finished activated

carbon also depends essentially on the type of the activation methods and on the structural properties of the original precursor material [55].

3.1.3. Commercial forms of activated carbon

Commercial activated carbon is produced as powder (PAC), fibers (FAC), or granules (GAC) depending on its application. It regularly exhibits BET specific surface magnitudes between 500 and 2000 m^2/ g. However, the so-called "super-activated carbons" exhibit surfaces areas above 3000 m^2/ g. Activated carbon's macro, meso, and micropore volumes may range from 0.5 to 2.5 m^2 /g [56].

3.1.4. Applications of activated carbon:

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

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 cathode 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 [57].

In environment field activated carbon can be used for removal of poisonous heavy metal ions from aqueous solutions. Adsorption in this case is due to the surface complex formation between the metal ions and the acidic surface functional groups of AC. Adsorption is due to the surface complex formation between the metal ions and the acidic surface function group of AC. The removal efficiency is influenced by various factors, such as solution concentration, solution pH, ionic strength, nature of adsorbate, adsorbent modification procedure, Physical properties (surface area, porosity), and the chemical nature of AC [58].

In medical applications activated carbon is used to treat poisonings and overdoses following oral drug 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, instead of other decontamination methods such as ipecac-induced emesis or stomach pumping [59].

3.1.5. Surface characteristics and chemistry of activated carbon in this research

Activated carbon has unique characteristics; its high adsorption capacity is related to the porous structure and chemical characteristics. These characteristics determine its interaction with polar and non-polar compounds. It also has active edge sites that determine its chemical reaction nature. Therefore, the adsorption phenomena can't be only explained in relation to surface texture including surface area and pore size distribution, but a combination of both surface and chemical characteristics of activated carbon**.**

- **Scanning electron microscope analysis (SEM):**

The main features of the SEM are an electron source which provides the electrons that interact with the material to be examined, an arrangement of metal apertures, magnetic lenses and scanning coils or deflectors plates that confines, focuses and turns the beam of electrons into a thin and focused

monochromatic beam which is accelerated towards the sample and which irradiates the specimen in a raster fashion [60].

The interaction of the electrons with the specimen initiates a number of reactions inside the sample which results in the generation of signals which are taken advantage of to gain information about the sample. The SEM imaging process involves four major steps. These include sample preparation, the specimen scanning process, image formation and image analysis. The kind of preparation required of the sample depends on whether it is electrically conducting or not. Electrically conducting samples, for instance metals, only require minimal sample preparation prior to mounting on a sample stub for scanning and imaging. Non-conductive specimens such as activated carbons, however, must first be made conducting before mounting for study. Otherwise, these tend to charge when scanned by the electron beam leading to scanning faults and other image artifacts. Non-conducting samples are therefore first sputter coated with an ultra-thin coating of an electrically-conducting material before imaging. Other reasons for coating the sample surface are to increase the signal and surface resolution, especially with samples of low atomic number. Some of the commonly used materials for coating samples include gold, graphite, platinum, chromium, tungsten, osmium, and indium. For biological materials it is possible to increase the conductivity without coating by impregnating them with osmium before imaging. It is also possible to image non-conducting specimen without coating by using the Environmental SEM (ESEM) or the field emission gun (FEG) SEM [61].

- **Iodine value of the activated carbon:**

To investigate the porous structure of activated carbon, iodine adsorption from liquid phase was adopted by some researchers, in the characterization of sludge-based activated carbons. The adsorption of aqueous iodine is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm [62].

The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02 N iodine solution, was measured according to the procedure established by the American Society for Testing and Materials. The mean values of data for each experiment were presented , standard deviation was calculated from triplicate samples.

Iodine Number is accepted as the most fundamental parameter used to characterize activated carbon performance. It gives the measure of activity level (higher number indicates higher degree of activation) [63].

Iodine number indicates the micro pore (0 – 20 Å) content, reagents used in the iodine value test are as listed below:

- 0.1N Iodine solution (12.7 g iodine in 1 Liter of Distilled water).
- 0.05N Sodium thiosulphate pentahydrate solution (12.5 gm $Na_2S_2O_3.5H_2O$ in 1 liter distilled water)
- 1% Starch solution freshly prepared

❖ Activated carbon

Procedure of the iodine value test:

(I) Standardization of Iodine solution

* 10c.c of 0.1N Iodine solution was taken in conical flask.

* 2 drops of Starch solution was added to it.

* The pale yellow colour of Iodine Solution turned Blue.

* Titration of the formed solution was done with 0.05 N Sodium thiosulphate till it becomes Colorless.

* Burette reading corresponds to blank reading.(B)

(II) Activated carbon testing:

* 0.2 gm of Activated carbon was weighed very accurately.

* It was introduced into the Iodine flask which should be completely dry .

* 40cc of 0.1N Iodine solution was then added.

* The flask was shaken properly for 4 minutes and then filtered.

* The filterate was collected in a dry flask and then 10cc of the filtrate was titrated against standard Sodium thiosulphate solution using starch as indicator.

Burette reading corresponds to (A)

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 10 / Wt. of carbon x Blank reading(B)

C=B-A

- **BET –Surface area of activated carbon**

The surface area of activated carbon can be precisely determined by measuring the adsorption isotherm for nitrogen gas molecules and analyzing results using the Brunauer-Emmett-Teller (BET) isotherm equation (1938). BET model is mostly used in surface area measurement of amorphous material due to its simplicity, and accommodation with different adsorption isotherm types .The BET model extends the monolayer Langmuir model to multilayer adsorption. It assumes that the surface is homogeneous and that the different layers of molecules do not interact; in addition, forces of attraction between adsorbed molecules are neglected. Each adsorbed molecule in the monolayer is assumed to be an adsorption site for second layer of molecules, and so on. The relative pressure increases, until bulk condensation occurs [64] .

- **Fourier Transform Infrared Spectroscopy (FT-IR) :**

FT-IR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The

term Fourier Transform Infrared Spectroscopy (FT-IR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR is commonly used to identify chemicals from spills, paints, polymers, coatings, drugs and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compound. Several infrared spectral libraries including on-line computer libraries, to identify materials [65].

The surface functional groups anchored within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the matters considered . So many researchers focused on how to modify as well as to characterize the surface functional groups of carbon materials in order to improve or extend their practical applications .The heteroatom on the surface of activated carbon took significant role on its application. The heteroatom of porous carbon surface mainly contained oxygen, nitrogen,

hydrogen, halogen, etc, which bonded to the edges of the carbon layers and governed the surface chemistry of activated carbon. Among these heteroatom, the oxygen-containing functional groups (also denoted as surface oxides) were the widely recognized and the most common species formed on the surface of carbons, which significantly influenced their performance in sensors [66].

3.1.6. Adsorption Process definition

Adsorption is attachment or accumulation of fluid particles on pores of surface, but absorption is taken fluid molecules by liquid or solid and distribution throughout them. The substance that adsorbs is the adsorbate and the underlying material is the adsorbent or substrate. The process of adsorption involves separation of substance from one phase accompanied by its accumulation or concentration at the surface of another. Separation occurs due to differences in molecular weight, shape or polarity. These differences cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The reverse of adsorption is desorption [67].

3.1.6.1. Adsorption versus absorption.

Absorption is a physical or chemical process in which the molecules of one phase are uniformly interpenetrated among those of the other some bulk phase: gas, liquid or solid material to form a solution [68] .While in

adsorption molecules of one phase are present at the surface of the second phase; the difference is illustrated in (Fig 3.1).

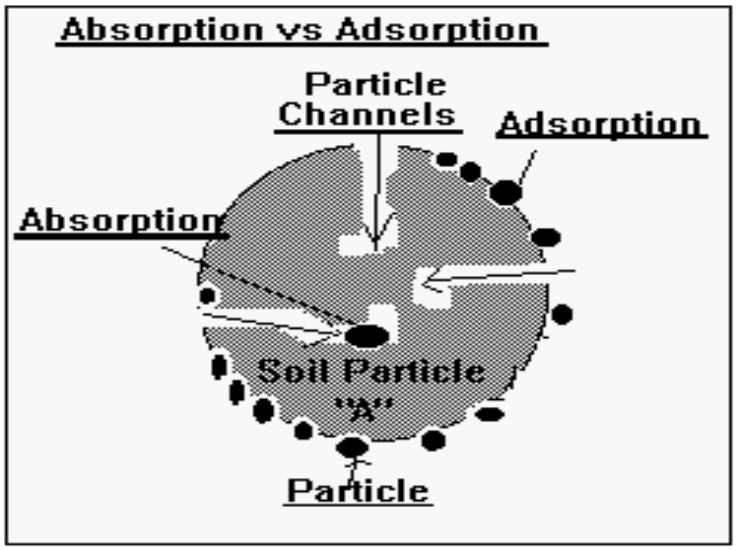


Figure 3.1 : Adsorption versus absorption

3.1.6.2. Adsorption mechanism

Adsorption process is one of the methods that used to remove contaminants such as pharmaceuticals, heavy metals and others from water. Other conventional processes for removing these compounds include extraction, steam distillation, bacterial and chemical techniques, oxidation with ozone/hydrogen peroxide ion-exchange electrochemical oxidation reverse osmosis and photo catalytic degradation. Among the unit operations in water and waste water treatment, adsorption technique remains widely preferred due to its simplicity of design and operation initial cost, flexibility and, ease of operation and insensitivity to toxic pollutants. Moreover, adsorption does not result in the formation of harmful substances [69].

In adsorption process atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent hold molecules atoms and therefore can attract and of contacting adsorbate. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physical adsorption (physisorption): a weak interaction mainly due to Vander Waals forces or chemical adsorption (chemisorption): interaction between the adsorbate and adsorbent's surface is strong characterized by electronic bonds (e.g. ionic or covalent) [70].

3.1.6.3. Adsorption isotherms

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature.

The most frequently isotherms used in describing the non-linear equilibrium are: Langmuir isotherm, Freundlich isotherm and Brunauer Emmett and Teller (BET) isotherm [71]. We will follow in this research the two following adsorption isotherm models:

- **Langmuir Isotherm**

In1916, Irving Langmuir was the first to develop a theoretical isotherm to describe the reaction between adsorbed gases above a solid surface at a fixed temperature; he was awarded Nobel Prize in chemistry for his work.The Langmuir isotherm, originally derived for the adsorption of gas

molecules on solid surfaces, was modified to fit the adsorption isotherm of solutes onto solid surfaces in solution systems.

Assumptions of Langmuir Model:

1- Monolayer adsorption: at maximum adsorption each site of free surface adsorbent can be occupied only by one adsorbate molecule, no deposition of adsorbate.

2- Identical adsorbent surface: adsorbent has a uniform surface and all sites are energically equivalent, so adsorption occurs through the same mechanism.

3- Adsorption is localized: when a molecule adsorbed at a given site it is independent on the occupation of neighbouring sites, no movement of the adsorbate on the surface of adsorbent, but molecule can be desorbed to solution (a reversible process).

Langmuir equation (1.1) is given as follows:

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{bqm} + \frac{Ce}{qm} \qquad (1.1)$$

Where qe is the amount of DCF adsorbed per unit mass of activated carbon (mg/g) at equilibrium, qm is the maximum amount of DCF adsorbed per unit mass of activated carbon (mg/g), Ce is the equilibrium concentration of the DCF (mg/L), and b is the Langmuir constant (L/mg).

The Langmuir isotherm model which is based on the assumption of a homogeneous adsorbent surface with identical adsorption sites [72].

- **Freundlich Isotherm**

In 1914, Freundlich popularized and justified theoretically another adsorption isotherm model , so known with his name. this assumption is given in the following equation (1.2) :

$$\log q_e = \log KF + \frac{1}{n} \log C_e \qquad (1.2)$$

Where Ce is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g) at equilibrium, KF and n are Freundlich constants. n giving an indication of how favorable the adsorption process is. K_f has unit of ((mg/g) (L/mg).

(1/n) is related with adsorption capacity of the adsorbent. The slope (1/n) ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as it is value gets closer to zero [73] .

3.1.6.4. Adsorption kinetic models

Adsorption kinetics study is important, since they give information about the adsorption system behavior and the rate at which specific constituent removed using certain adsorbent. In addition, they provide information about whether the adsorption process is chemical or physical and which specifically is the rate limiting step. There is several models that describe

the adsorption process. In this research we will use adsorption reaction models, which are classified into :

- **Pseudo-first order kinetic models**

A pseudo-first order kinetic model is considered as the earliest model developed to the kinetic process of adsorption. The final integrated form equation of this model as follows:

$$\log(qe - qt) = \log qe - \frac{k1}{2.303}t \tag{1.3}$$

Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at time t (min), respectively. k1 (min^{-1}) is the pseudo-first order rate constant [74].

- **Pseudo-second order kinetic models**

  This model is commonly employed to describe the adsorption of metal ions and polar functional group such as, ketones, aldehydes, dyes, herbicides, and phenolic compounds from aqueous solution assuming that Langmuir equation applies. The linearzed integral form of the model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{1.4}$$

Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at time t (min), respectively K_2 is the rate constant (g/(mg.min)) [75].

- **Second order kinetic models**

The typical form of second order rate equation can be applied to describe the adsorption process based on adsorbate uptake rate. The integrated forms of this equation as follow :

$$\frac{1}{C_t} = k_2^* t + \frac{1}{C_0} \tag{1.5}$$

Where C_0 and C_t (mg/L) is the concentration of solute at t=0 and at time t (min), respectively, and K_2*(L/(mg.min) is the rate constant [76].

- **Intra-particle diffusion model**:

In a liquid-solid system, the theory proposed by Weber and Morris to link the fractional uptake of solute on particles varies proportionally here with $t^{1/2}$.

The Weber and Morris equation is:

$$q_t = k_b t^{1/2} + A \tag{1.6}$$

q_t (mg/g), K_b (mg/g $min_{1/2}$) is the rate constant of intra-particle diffusion and (A) gives an idea about the thickness of the boundary layer. The value of kb will be calculated from the slope of the resulting curve[77].

3.1.7. Diclofenac sodium overview

Diclofenac sodium (sodium 2-[2,6-dichlorophenylamino]phenyl]acetate), is a white or slightly yellowish, crystalline powder, which slightly hygroscopic, sparingly soluble in water, freely soluble in methanol, soluble in alcohol, slightly soluble in acetone. It melts at about 280 °C, with decomposition.

It is a non-steroidal anti-inflammatory drug (NSAID) which is widely used in human medical care as analgesic, antipyretic, anti arthritic and anti rheumatic compound [78].

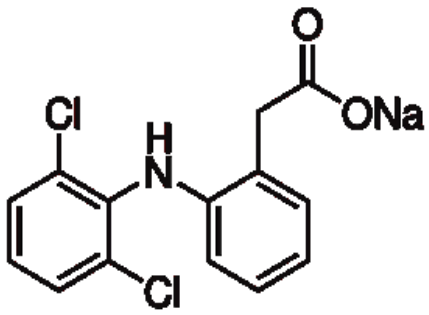


Figure (3.2): The structural formula of diclofenac sodium

- **Mechanism of action:**

The exact mechanism of action is not entirely known, but it is thought that the primary mechanism responsible for its anti-inflammatory, antipyretic, and analgesic action is inhibition of prostaglandin synthesis by inhibition of cyclooxygenase (COX-1). Inhibition of COX also decreases prostaglandins in the epithelium of the stomach, making it more sensitive to corrosion by gastric acid. This is also the main side effect of diclofenac. Diclofenac has

a low to moderate preference to block the COX2-isoenzyme (approximately 10-fold) and is said to have therefore a somewhat lower incidence of gastrointestinal complaints than noted with indomethacin and aspirin [79].

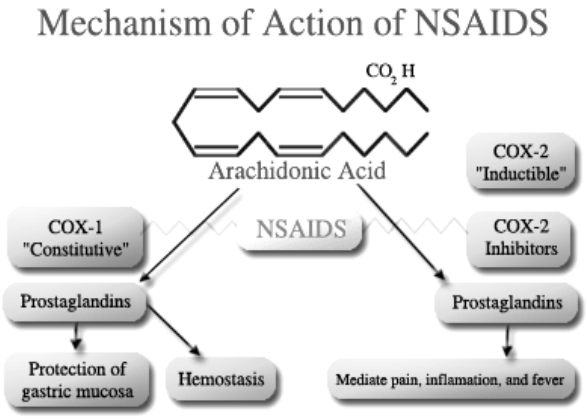


Figure (3.3) : DCF mechanism of action

- **Side effects:**

Gastrointestinal experiences including: abdominal pain, constipation, diarrhea, dyspepsia, flatulence, gross bleeding/perforation, heartburn, nausea, GI ulcers (gastric/duodenal) and vomiting. Abnormal renal function, anemia, dizziness, edema, elevated liver enzymes, headaches, increased bleeding time, pruritus, rashes and tinnitus. fever, infection, sepsis, congestive heart failure, hypertension, tachycardia, syncope, dry mouth, esophagitis, gastric/peptic ulcers, gastritis, gastrointestinal bleeding, glossitis, hematemesis, hepatitis, jaundice, eosinophilia, leukopenia, melena, purpura, rectal bleeding, stomatitis, thrombocytopenia, weight changes, anxiety, asthenia, confusion, depression, dream abnormalities,

drowsiness, insomnia, malaise, nervousness, paresthesia, somnolence, tremors, vertigo, asthma, dyspnea, alopecia, photosensitivity, sweating increased, blurred vision, cystitis, dysuria, hematuria, interstitial nephritis, oliguria/polyuria, proteinuria, renal failure [80].

3.1.7.1. Environmental impact of diclofenac sodium (DCF)

In recent years, diclofenac was found as an environmental contaminant in sewage, surface, ground, and drinking water samples. In long-term monitoring investigations of sewage was identified as one of the environmentally most important pharmaceutically active compounds (PhACs) present in the water cycle at concentrations up to the mg/l level. No significant removal of diclofenac is observed during municipal sewage treatment [81].

- **Sources of this pharmaceutical in environment**

In spite of all benefits of these drugs in the treatment of many diseases for human and animals, but if they were added to the environment in large quantities, special interest will be needed. Through several sources this pharmaceutical will be found that include:

1. Direct disposal at manufacturing.
2. Excretion with urine and feces (sewage water).
3. Drugs in animal manure [82].

3.1.7.2. Recent researches on diclofenac sodium (DCF) removal from aqueous solution

Different trace pollutants and often enough some of these pollutants leave the Sewage treatment plant unaffected. Some advanced water clarification techniques, as ozonation, membrane bioreactors or coagulation/flocculation and flotation, have been brought into discussion to improve the removal of these trace pollutants like diclofenac [83].

Silica gel synthesized by sol-gel process was used as an adsorbent for removal of diclofenac from contaminated water [84].

Carbamazepine and diclofenac removal was studied in waste water treatment plants and occurrence in water bodies leading to that they don't cause acute environmental toxicity but their chronic effects needs attention, their chemical, physical and pharmacological properties are also addressed in context, which can largely influence their environmental behavior [85].

Karaman et.al studied removal of diclofinac from waste water using clay-micelle complex which is positively charged, have large surface area and include large hydrophobic domains so it was an efficient method for adsorption [86].

3.1.7.3. Eucarbon®

Eucarbon® tablet was developed in 1909 by the pharmacist Mag. F. Trenka and by Prof. Dr. W. Pauli, tablets contain a combination of

anthranoid drugs (Senna and Rhubarb), Sulfur, and the adsorbent Vegetable Charcoal (carbo ligni) produced in accordance with GMP-Standards.

This formula is used for treatment of entire digestive system conditions, especially due to its spasmolytic effect, relieving of gas pains and detoxifying activity (by adsorbing toxins) from GI- tract.

Also charcoal from Carbo Ligni together with Senna leaf und Rhubarb extract is a very useful medicine, for treatment of constipation especially in high doses. Figure (3.4) showed this mediciene as available in the market [87].

Figure (3.4) : Eucarbon® mediciene

3.2. Experimental set-up

3.2.1 Materials

3.2.1.1 Precursor:

The residual cyclamen tubers tissues remained after extraction of saponin glycosides were used as the precursor for preparation of activated carbon by physical activation method. This powder was washed many times with distilled water , dried at 110 ºC in oven and then sieved through mesh # 18 to #30 to get rid of the remaining pulp and skin.

3.2.1.2 Activators:

- Phosphoric acid H_3PO_4
- Potassium hydroxide KOH
- Zinc chloride $ZnCl_2$

All of 98% purity were used as chemical reagents for activation of cyclamen tubers powder.

3.2.1.3 Furnace:

Tubular regulated furnace (Lindberg 9001) with a 0.25 cm thick cylindrical stainless steel tube (4 cm inner diameter and 74 cm length).

3.2.1.4 Adsorbate and Chemicals

Diclofenac sodium (DCF) (molecular weight = 318.1 g /mol; chemical formula = $C_{14}H_{10}Cl_2NNaO_2$; pKa = 4.2) was purchased from Jerusalem pharmaceutical company Ramallah – Palestine.

All other chemical used such as hydrochloric acid, sodium thiosulfate, iodine and sodium hydroxide were of analytical grades.

3.2.1.5 FT-IR analysis

Nicolet iS5 FT-IR Spectrometer was used for the detection of functional groups in the prepared activated carbon samples.

3.2.2. Activation process

3.2.2.1 Physical activation

In this process, the char produced from carbonization step is activated using carbon gaseous activating agent N_2 gas. Oxidation reaction takes place between the carbon atom and the gas; increasing the number of pores in the carbonaceous structure. This process is environmental friendly as no chemical polluting agents are engaged in the process; still it has several drawbacks represented in the low carbon yield and high energy consumption.

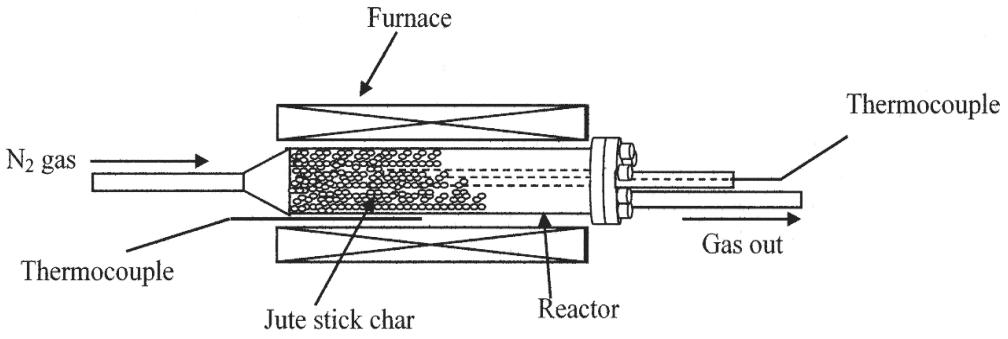


Figure (3.5) : Tube furnace scheme

Longer carbonization/ activation time and higher temperature are required to produce activated carbon with the same characteristics obtained in the chemical activation . 30 g of dried cyclamen is placed in a flat crucible and inserted in the center of calibrated furnace.The carbonization/activation program is set according to Table (4.3).

Table (3.1): carbonization/activation program set-up

Value	Parameter
550 °C	Activation temperature
20 °C/min	Heating rate
70 min	Holding time
0.2 L/min	N_2 flow rate

3.2.2.2. Chemical activation

Chemical activation produces highly porous activated carbon by impregnation of the precursor with the following chemical activating agent; potassium hydroxide (KOH), phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$). These chemical agents have dehydrating properties that influence the pyrolytic decomposition and prevent the formation of tars and volatile

organic compounds during activation at high temperature .As a result; higher activated carbon yield is obtained.

- **impregnation by Phosphoric Acid**

Phosphoric acid solution (100 mL, 50% w/w) was used in chemical activation of cyclamen persicum Tubers. The solution was added to the 30g sample and the mixture was thoroughly stirred at 85°C for 2 h.

After this impregnation procedure, the solution was filtered to separate the residual acid. Then cyclamen tubers were then washed with deionized water, dried in an oven at 110°C, before carbonization at 450°C for 50 min. After carbonization, the product was washed with hot deionized water and then with cooled deionized water until pH of the filtrate became 6. The product was then dried in an oven at 110°C and stored for further use.

- **Carbon Activation by Zinc Chloride**

A sample of 25g Cyclamen persicum tuber powder was mixed by stirring with zinc chloride solution (100 mL, 20 % w/w).

In this work, impregnation with zinc chloride was carried out at 70°C in awater bath until excess water evaporated. Then the sample was filtered and dried after washing with distilled water at 110°C in an oven. then carbonized at temperature 450°C for 50 min. The carbonized product was washed with 0.50 M hydrochloric acid solution, then with distilled water

and cooled, to remove residual inorganic activating agent. The final product was dried in an oven at 110°C and stored for further use.

- **KOH impregnation of cyclamen tubers**

A sample of 15g dried cyclamen tuber powder was mixed with KOH at ratio (1: 0.5) weight by weight . The solid mixture is placed in 500 ml round bottom flask, where 300 ml of distilled water is added. The solution is refluxed for 2 hrs at 60 °C, left to cool and then decanted. The wet solid is then dried in the oven for 1 hr at 110 °C. The impregnated sample is carbonized and activated under 450 °C temperature for 50 min.

3.2.2.3 Percentage Yield of the prepared activated carbon

The yield of each activated carbon sample was calculated as follows:

$$\text{Yield of activated carbon (wt \%)} = \frac{weight\ of\ activated\ carbon}{weight\ of\ \text{CT powder}} \times 100$$

3.2.3. Adsorption kinetic and thermodynamic of diclofenac sodium (DCF) onto (CTAC) experiment

3.2.3.1. Determination method of diclofenac Sodium Concentration

Diclofenac Sodium (DCF) concentration was determined by a standard method called "Ultraviolet Spectrophotometric Screening Method".

Diclofenac sodium concentration was spectrophotometrically measured on UV-visible spectrophotometer Shimadzu- Model No: UV-1601, double

beam spectrophotometer wave length range 190-1100 nm, accuracy ± 0.004. For Diclofenac sodium, maximum absorbance at 276 nm was observed against distilled water background.

3.2.3.2. Diclofenac sodium Standard solutions preparation

Diclofenac sodium stock solution (1000 mg/L) was prepared by dissolving 1.02 g in 100 ml distilled water then diluting to 1.00 L with distilled water, this intermediate solution was used to prepare different calibration standard solutions with concentrations in the range 0.0-50 mg/L diclofenac sodium. Calibration curve was constructed by plotting value of net absorbance vs concentration of standard diclofenac sodium (DCF) solution. For comparison purposes, adsorption behaviors of activated carbons prepared here and Eucarbon drug were studied.

The initial and final concentrations of DCF were measured. The amount of adsorption at equilibrium, qe (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)\,V}{W} \tag{3.1}$$

The removal percentage of diclofenac sodium (DCF) was calculated using the following equation:

$$PR\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{3.2}$$

Where C_0 and C_e are initial and equilibrium DCF concentration respectively.

3.2.4. Adsorption experiment

3.2.4.1. Effect of Adsorbent Dosage

Different amounts (0.10-0.80 g) of activated carbon from cyclamen tubers and Eucarbon drug were placed into conical flasks, then solutions (50 mL, 50 mg/L Diclofenac sodium) were added to each flask and the pH was adjusted to 4. The mixtures were then shaken for 1.5 h at 25°C.

3.2.4.2. Effect of Initial pH

Effect of initial pH on adsorption was investigated in the pH range 2-12. The pH was varied as desired, by adding sodium hydroxide or sulphuric acid solutio. Diclofenac sodium (DCF) solutions (50 mL,50 mg/L each) were added to adsorbent samples (0.25 g). The mixtures were then shaken for 1.5 h at 25°C.

3.2.4.3. Effect of Temperature

The effect of temperature on adsorption was studied. Diclofenac sodium solutions (50 mL, 50 mg/L each) were added to adsorbent samples (0.25 g) at pH 4. The mixtures were shaken for 1.5 h at different temperatures in the range 15-45°C.

3.2.4.4. Effect of contact time (Kinetic study)

The effect of time on adsorption was studied. Diclofenac sodium solution (50 mL, 50 mg/L) was added to adsorbent sample (0.25 g) at pH 4. The mixture was shaken at 25°C .

Aliquots (1 mL each) of the clear solution were pipetted out at different time intervals until equilibrium was reached after 24 h.

3.2.4.5. Effect of diclofenac sodium (DCF) concentration

In each adsorption experiment, different concentration ranging from 20 to 80 mg/L Diclofenac sodium was added to 0.25g adsorbent, with initial pH 4. The flasks were shaken at 25°C for 150 minute to reach equilibrium.

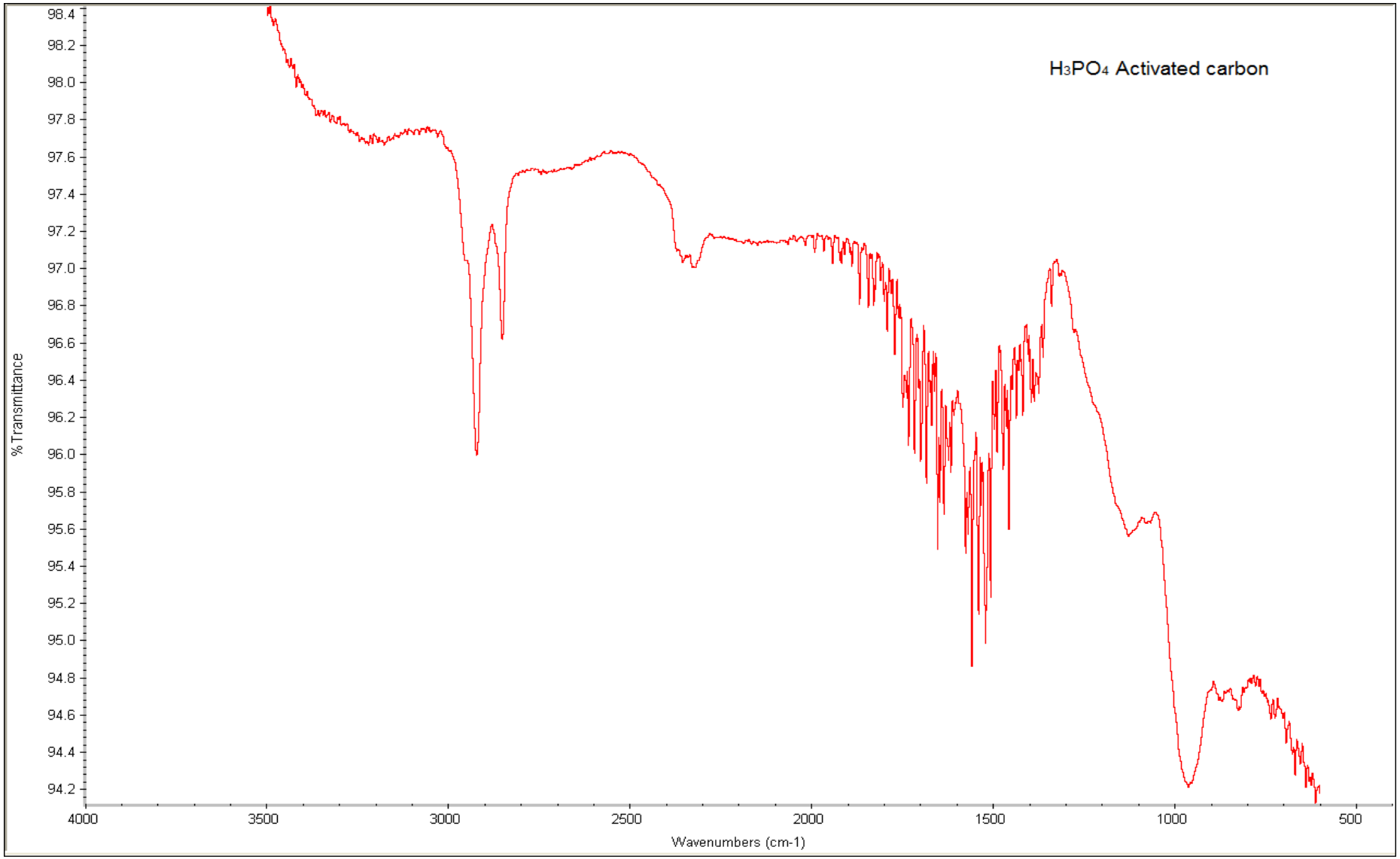
The initial and final concentrations of DCF were measured. The amount of adsorption at equilibrium, qe (mg/g), was also calculated .

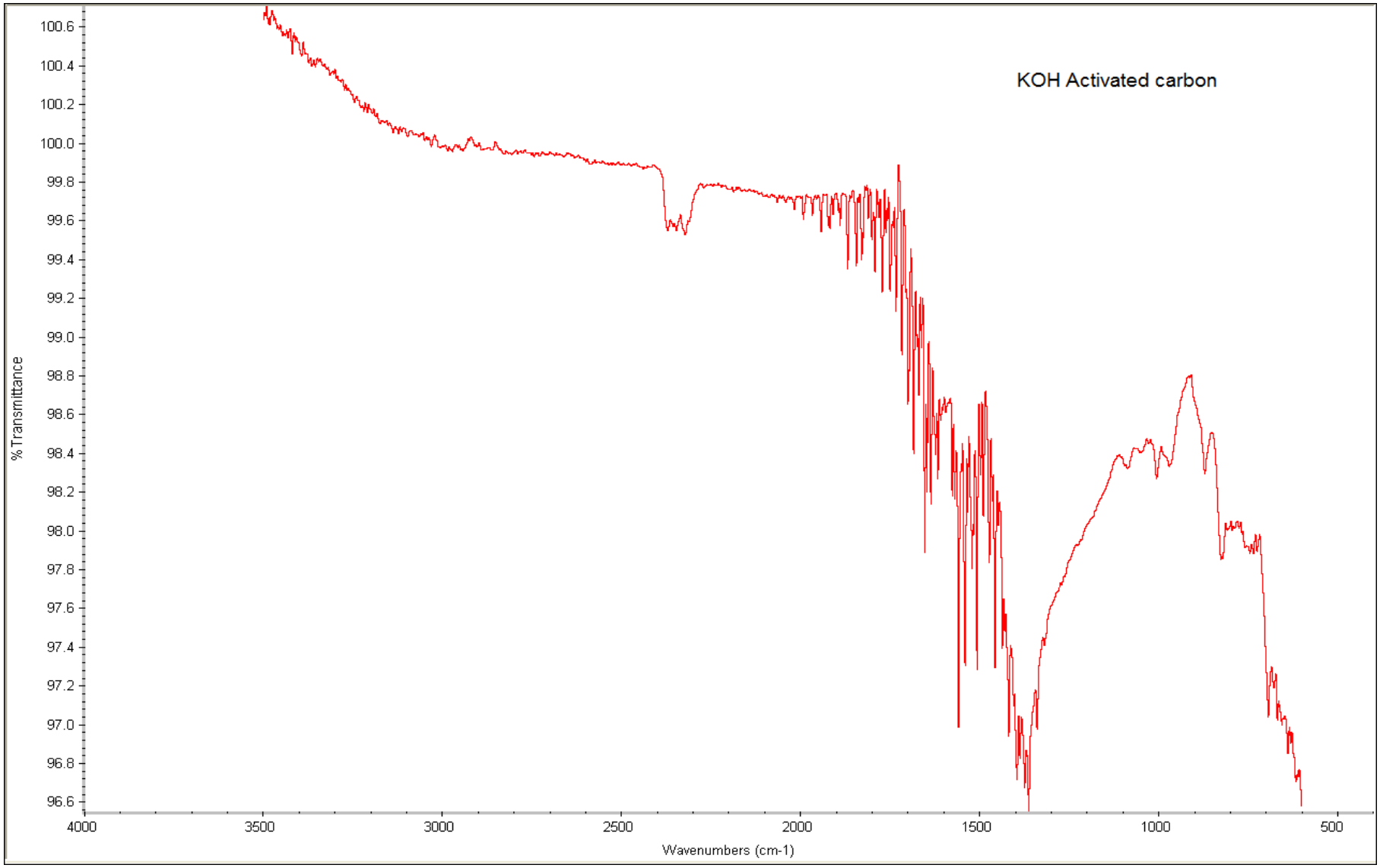
3.3 Results and discussion

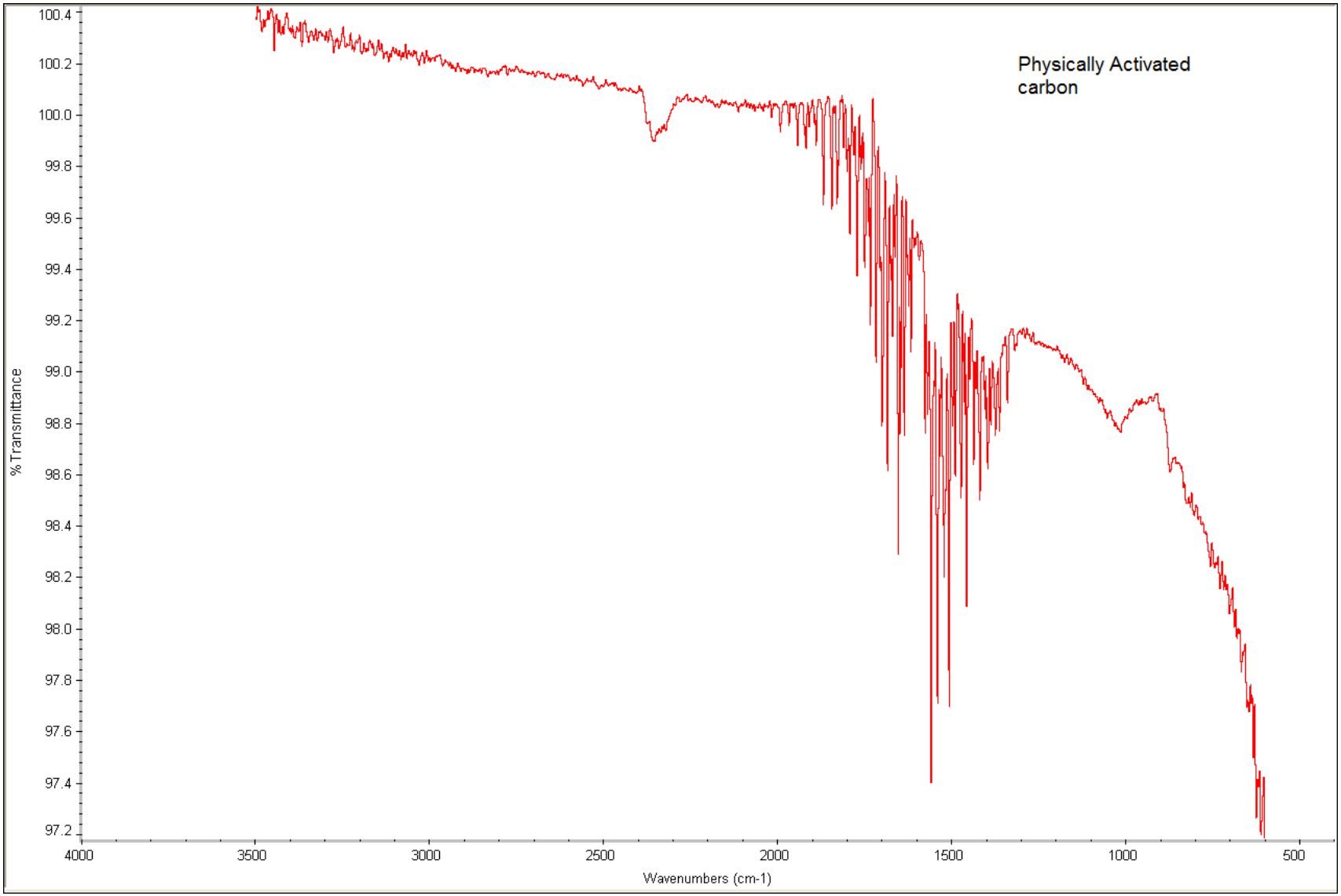
3.3.1 FTIR analysis of activated carbon samples

In these following figures FTIR analysis revealed the functional groups for each prepared AC samples and Eucarbon drug for comparison.


ZnCL2 Activated carbon
% Transmittance
100.8
100.6
100.4
100.2
100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


H3PO4 Activated carbon
% Transmittance
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
96.4
96.2
96.0
95.8
95.6
95.4
95.2
95.0
94.8
94.6
94.4
94.2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


KOH Activated carbon
% Transmittance
100.6
100.4
100.2
100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


Physically Activated carbon
% Transmittance
100.4
100.2
100.0
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

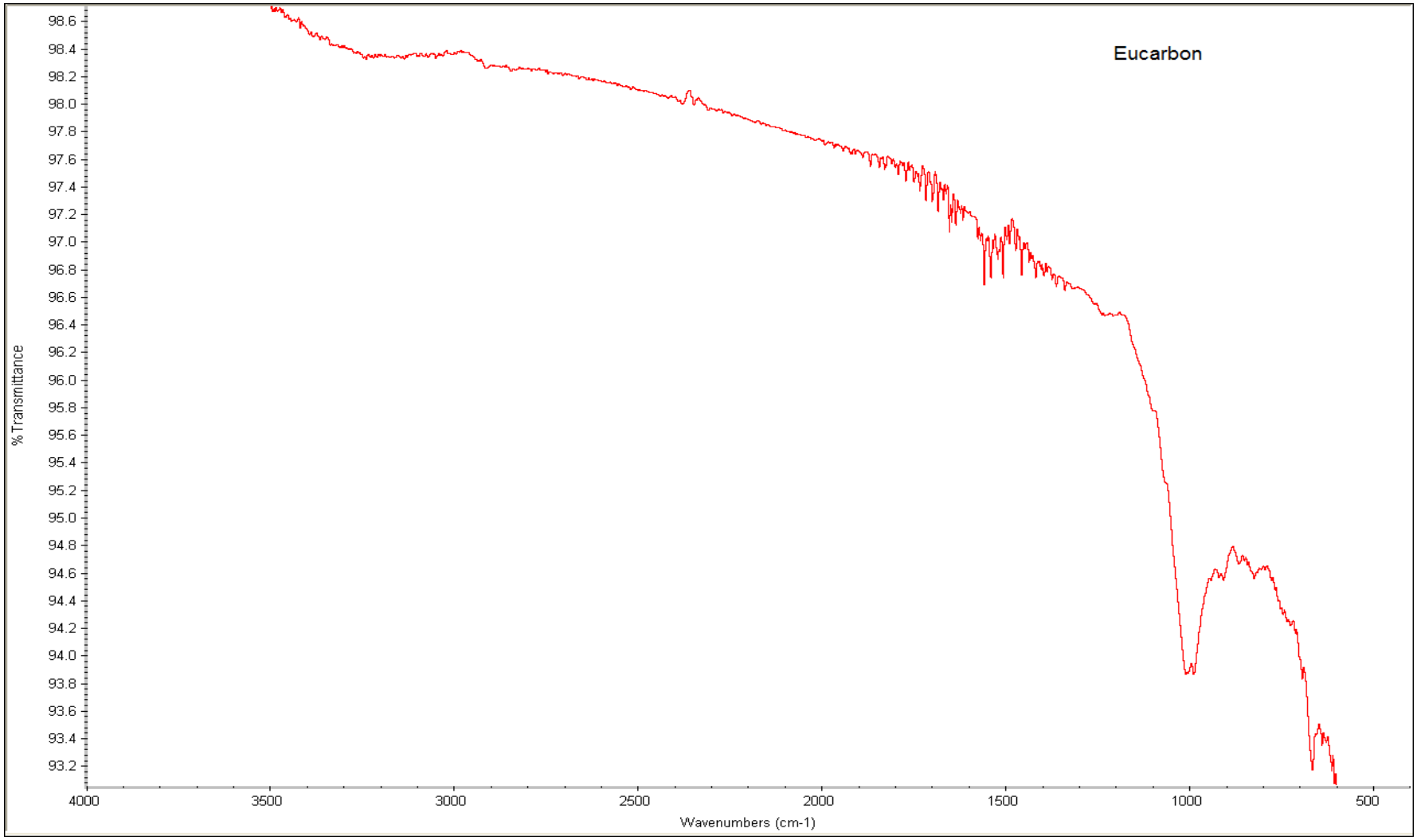


Figure (3.6) : FTIR analysis for activated carbon samples and Eucarbon

FT-IR spectra of activated carbon prepared from cyclamen tubers by different activation methods was interpreted using of the FTIR spectra – library references to reveal the existence of functional groups occurring in each structure. The bands at 2800 - 2980 cm^{-1} (C-H aliphatic stretching) and 1375 - 1465 cm^{-1} (C-H aliphatic bending) are more intense in H_3PO_4 and KOH activated samples .The band at around 1800 cm^{-1} denotes the existence of carbonyl/carboxyl groups and can be observed in H3PO4 but not in others.

The 1600-1500 cm^{-1} band, which is visible in H_3PO_4, KOH and physically activated samples indicated the presence of an aromatic C=C ring stretching .The bands observed at 1240-1000 cm^{-1} indicates the existence C-O stretching of phenolic, acids, ethers and esters and alcoholic groups, and were identified in the FTIR spectra of Eucarbon drug sample. 900-600 cm^{-1} Out of plane bending of C-H groups located at the edges of aromatic planes were defined in H3PO4 activated carbon sample.In all activated carbon samples produced from cyclamen tubers showed apeak at 2200-2400 cm^{-1} which indicates the presence of -C≡N group .

Zinc chloride as activating agent diminished most of the functional groups present in cyclamen tuber powder.

These functional groups can be summarized in table (3.2):

Table (3.2) : Functional groups of AC samples by FTIR analysis

Sample	Functional group
	Wave number (cm-1)
$ZnCl_2$	2200-2400 cm^{-1} -C≡N group
H_3PO_4	2200-2400 cm^{-1} -C≡N group 2800 - 2980 cm^{-1} (C-H aliphatic stretching, 1800 cm^{-1} carbonyl/carboxyl groups 900-600 cm^{-1} bending aromatic C-H 1600-1500 cm^{-1} aromatic C=C ring stretching.
KOH	2200-2400 cm^{-1} -C≡N group 1450-1300 cm^{-1} C-H vibrating alkene 1600-1500 cm^{-1} aromatic C=C ring.
Physical activation	2200-2400 cm^{-1} -C≡N group 1600-1500 cm^{-1} aromatic C=C ring stretching.
Eucarbon	1240-1000 cm^{-1} C-O stretching

3.3.2 Iodine number surface area :

As given in table 3.3 the best surface area of the produced activated carbon samples following iodine number test was by using zinc chloride as chemical activating agent which produced 606.78mglg followed by physical activation process that gave 522.07 mg/g surface area .For comparison Eucarbon drug had 592.62 mg /g using this iodine number test.

Table (3.3): surface area of different AC according to iodine number test.

Sample	Surface area (mg | g)
$ZnCl_2$	606.78
H_3PO_4	423.30
KOH	493.85
Physical activation	522.07
Eucarbon	592.62

For comparison the BET surface area for zinc chloride activated sample was 880.936 m^2 /g and for physically activated sample was 799.028 m^2 /g, this result indicated that iodine value was a good method for comparing the prepared samples of CTAC.

3.3.3. Scanning electron microscopic (SEM) of AC:

In figure 3.7 different scanning electron microphages for activated carbon samples were showed to indicate the effect of each method in activation process.

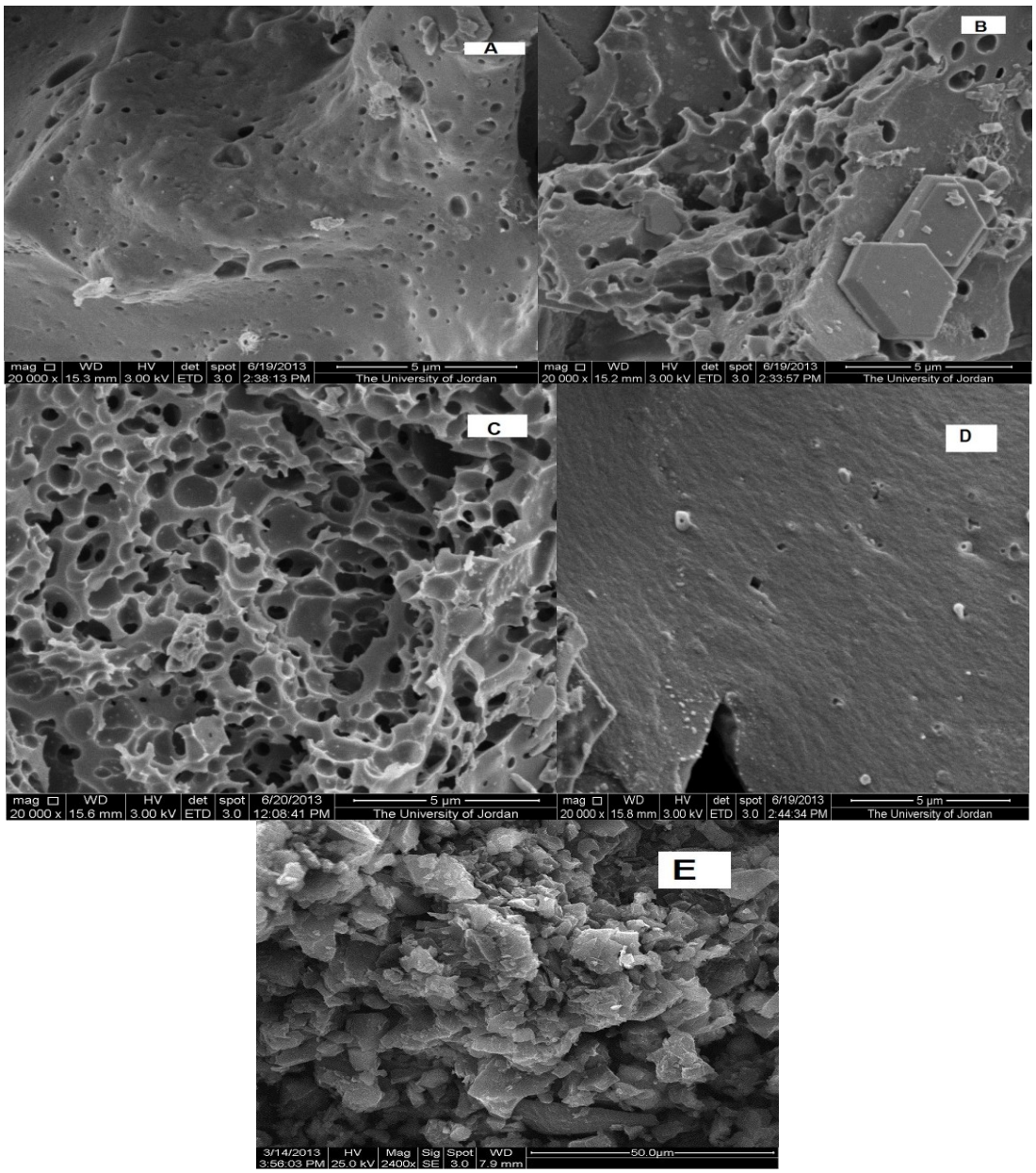


Fig (3.7): SEM micrographs of several types of the produced activated A (ZnCl2 / CTAC) , B (H3PO4 /CTAC) , C (KOH /CTAC) , D(physically CTAC) , E (Eucarbon®).

The external surface showed best porous structure in chemically activated carbon by potassium hydroxide (KOH) reagent as this surface was rich in pores, whereas the surface of the carbon activated physically has no porous structure except for some occasional cracks ; The porous structure of the prepared activated carbon by zinc chloride ($ZnCL_2$) and phosphoric acid (H_3PO_4) has less extent of porous structure comparing with potassium hydroxide; this can be explained as the evaporation of KOH during carbonization process would leave empty spaces on the carbon surface more than other chemical reagents. Eucarbon® sample showed multilayer structure that form sites for adsorption process on these layers but not pores.

3.3.4.Percentage yield of the prepared CTAC samples

The %Yield of the prepared activated carbon from cyclamen tubers was summerised in table (3.4) :

Table (3.4) : Percentage Yield of prepared activated carbon

CTAC sample	% Yield
$ZnCl_2$	45%
H_3PO_4	53%
KOH	40%
Physically activated	26.5%

3.3.5. Adsorption of diclofenac sodium on AC from cyclamen persicum tubers

UV-VIS spectrophotometry which was chosen and preferred to many other methods. That is due to its low pollution effects, simplicity, speed and suitability to indicate the kinetic change of the diclofenac sodium concentration. typical calibration curve for diclofenac sodium at 276 nm is shown in figure (3.8):

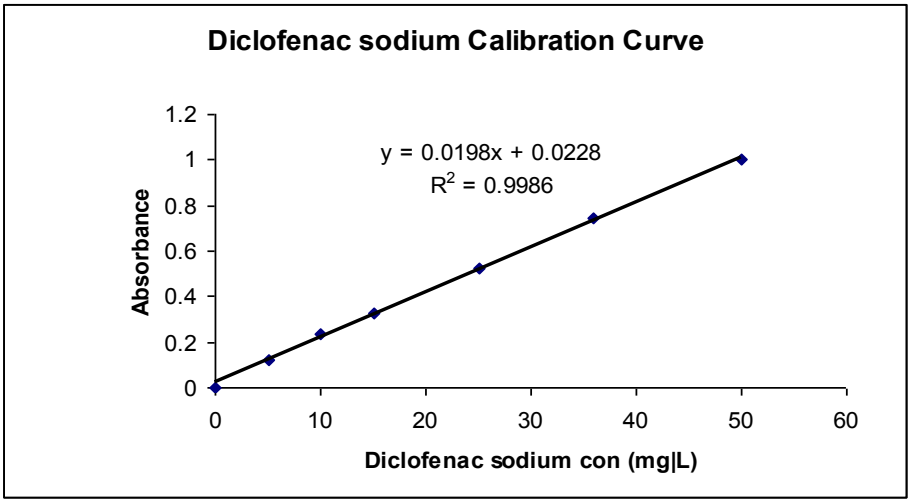


Figure (3.8) : A typical calibration curve for diclofenac sodium analysis by UV-VIS spectrometric method

3.3.5.1. Effect of Contact Time

The effect of contact time on removal percentage % of diclofenac sodium (DCF) was shown in Fig (3.9).

The adsorbed amount of DCF onto CTAC and Eucarbon® increases with the increase of contact time, as shown in Fig(3.9), and the DCF adsorption reached equilibrium in about 120 min for CTAC and 150 min for Eucarbon® . Adsorption capacity for DCF showed a rapid increase in

adsorbed amount during the first 15 min , while Eucarbon® showed this increase during 30 min. This fast adsorption capacity at the initial stage by CTAC indicated higher driving force that making fast transfer of DCF to the surface of CTAC particles comparing with Eucarbon®, this result indicated a significant effectivness in using CTAC as adsorbent than Eucarbon®. From this figure the % removal of DCF using CTAC was 72% while using Eucarbon® it was 70%.

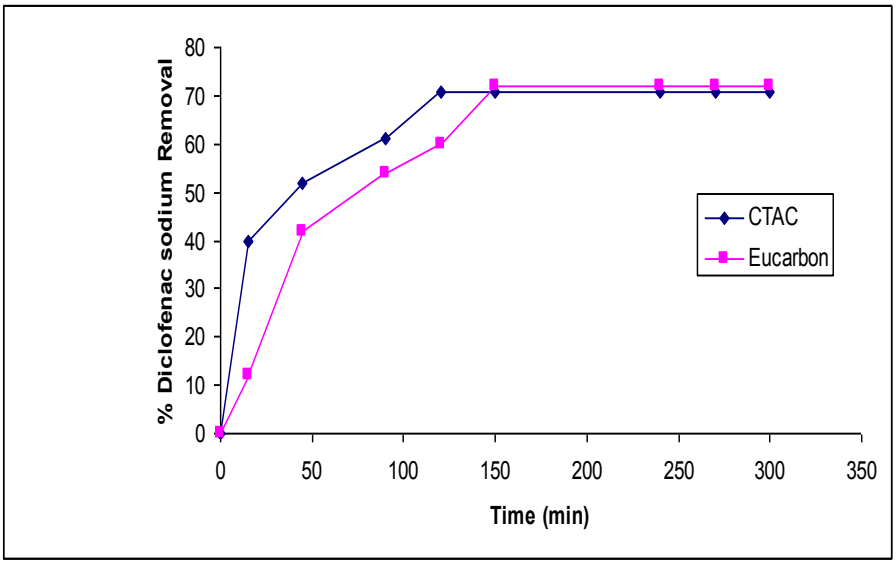


Figure (3.9) : Effect of contact time on diclofenac sodium(DCF) removal by CTAC and Eucarbon® at (initial conc. 50 mg/L, initial pH: 4, temperature: 25 ºC).

3.3.5.2. Effect of adsorbent dosage

The effect of CTAC and Eucarbon dosage on diclofenac sodium(DCF) removal was studied using 0.1 to 0.7g adsorbent dosage at an adsorption time of 120min to reach equilibrium. The results are summarized in Fig(3.10) The percent of DCF removal increased by increasing dosage for each type of adsorbents .

Adsorption increases up to 82% with adsorbent dosage of (0.7 g/50 mL) of CTAC and 76% with Eucarbon, because increasing adsorbent dosage at fixed DCF concentration provided more available adsorption sites and thus increased the extent of DCF removal.

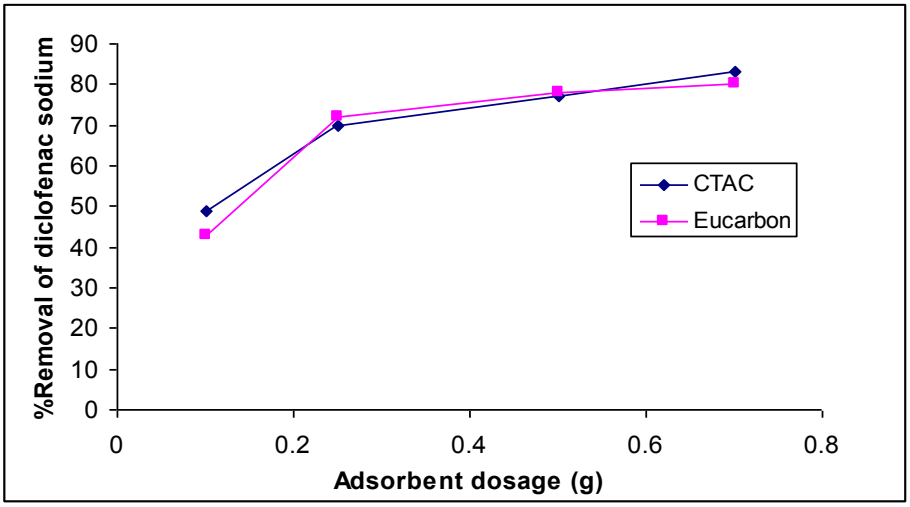


Figure (3.10): Effect of adsorbent dosage on diclofenac sodium removal by at (initial conc: 50 mg/L, initial pH: 4, temperature: 25 ºC and contact time: 120 min).

3.3.5.3. Effect of pH

The variation of adsorption onto CTAC and Eucarbon® was investigated in the pH range 2-12 using sulfuric acid and sodium hydroxide to control pH. The effect of pH on diclofenac sodium (DCF) removal was studied, using 0.25g CTAC and Eucarbon® at an adsorption time of 150 min to reach equilibrium, figure (3.11) (summarizes these results:

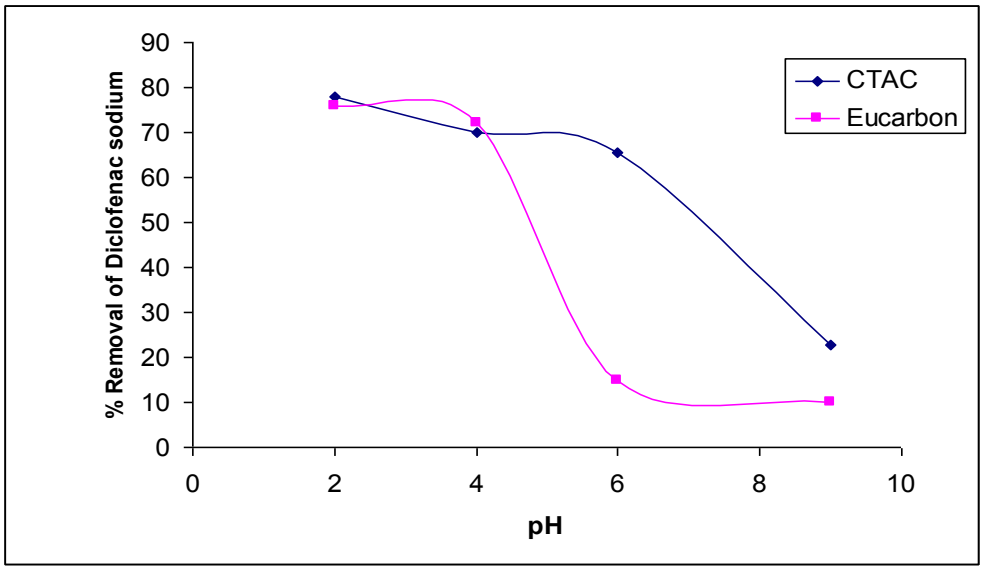


Figure (3.11): Effect of pH on diclofenac sodium removal by CTAC and Eucarbon® at (initial conc.50 mg/L, temperature: 25 °C, contact time: 150 min)

For each adsorbents, the optimal pH for the adsorption of diclofenac sodium (DCF) was 2, this result indicated pH less than the pKa of this pharmaceutical (pKa = 4.20), as DCF present in its neutral form, and its solubility in water decreases. So as pH decreases the vanderwal interaction between DCF and adsorbent surface increased by physical adsorption process.

3.3.5.4. Effect of Temperature

The effect of temperature on adsorption onto CTAC and Eucarbon was investigated in the range of 15-45 °C. The results were shown in Fig (3.12).

In this Figure, diclofenac sodium(DCF) adsorption decreased with increasing temperature. The highest percentage adsorption performance at 15 ºC which reach to 83.58 % by CTAC and 74% by Eucarbon.

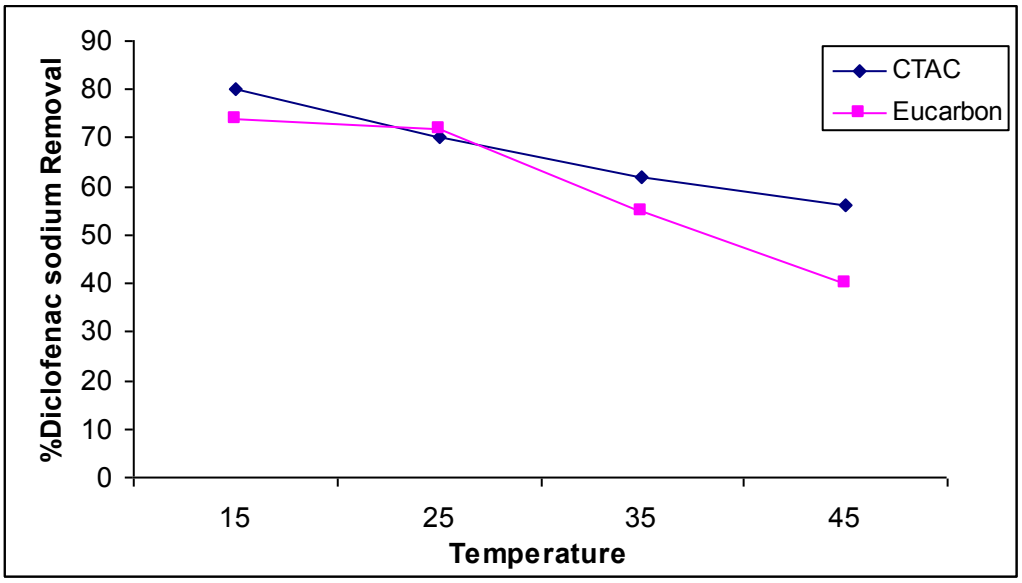


Figure (3.12): Effect of temperature on diclofenac sodium removal by CTAC and Eucarbon® at (initial conc. 50 mg/L, initial pH: 4, contact time: 120 min.

Thus, when temperature increased it caused an increase in water solubility of the DCF, which hindered its adsorption because the pharmaceutical would have more affinity with the solvent than with the adsorbent. The force of the attraction between the DCF and the adsorbents decreased as a function of increasing temperature because the increasing temperature caused an increase in the agitation of the dissolved chemical species, reducing its physical interaction with the adsorbent.

3.3.5.5.Effect of diclofenac sodium (DCF) concentration

Figure (3.13) shows the effect of initial concentration of diclofenac sodium(DCF) on the % removal at equilibrium. This figure shows that the increase of concentration increases the percentage of diclofenac sodium(DCF) removal, by CTAC and Eucarbon® .

As diclofenac sodium (DCF) concentration increases from 20 mg/L to 70 mg/L, the percentage removal was increased from 42 % to 81% for CTAC and from 30% to 77% for Eucarbon® .

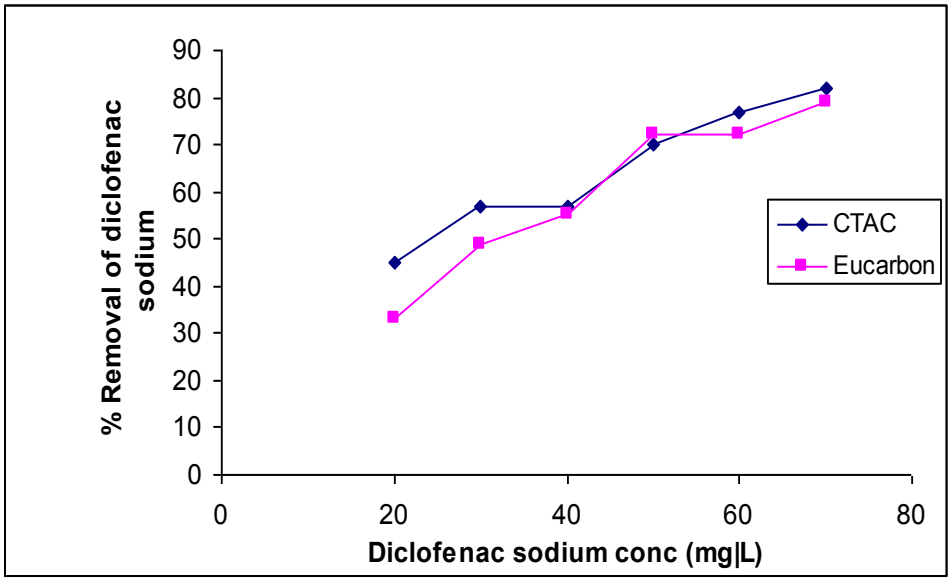


Figure (3.13) : Effect of diclofenac sodium (DCF) concentration on % removal by CTAC and Eucarbon® at (initial adsorbent dose: 0.25 g, initial pH: 4, contact time: 120 min, Temperature 25 ºC).

3.3.5.6. Adsorption isotherms

In this research, Langmuir and Freundlich isotherm models were used to describe the adsorption isotherm to study relationship between the amounts of diclofenac sodium (DCF) adsorbed (q_e) and its equilibrium concentration in solution at 25 °C onto CTAC (C_e) is given in Figure (3.14):

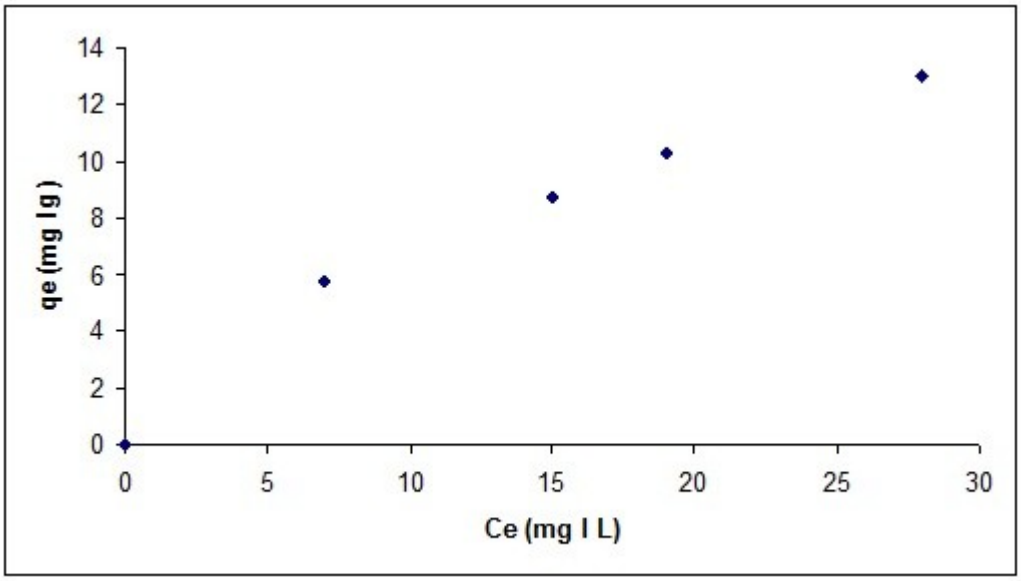


Figure (3.14): Equilibrium adsorption isotherm of DCF onto CTAC at (temperature: 25 °C, initial pH 4 and solid/liquid ratio 0.25 g/50 mL)

Adsorption isotherm for DCF onto CTAC at 25 °C using Languimer adsorption model is given in Figure (3.15) :

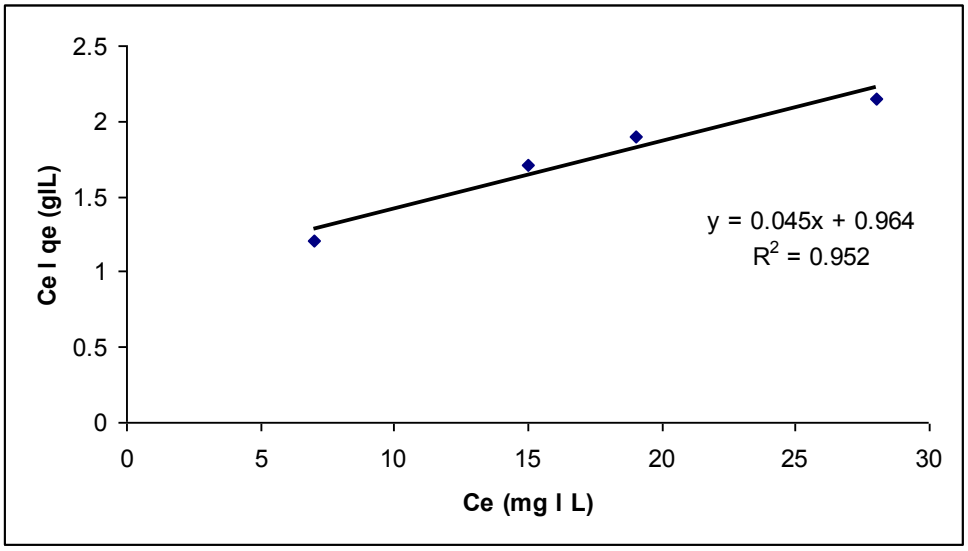


Figure (3.15): Langmuir plot for DCF adsorption onto CTAC at (Temperature; 25 °C, initial pH: 4 and solid/liquid ratio 0.25 g/50 mL)

Adsorption isotherm for DCF onto CTAC at 25 °C using Freundlich adsorption model is given in Figure (3.16) :

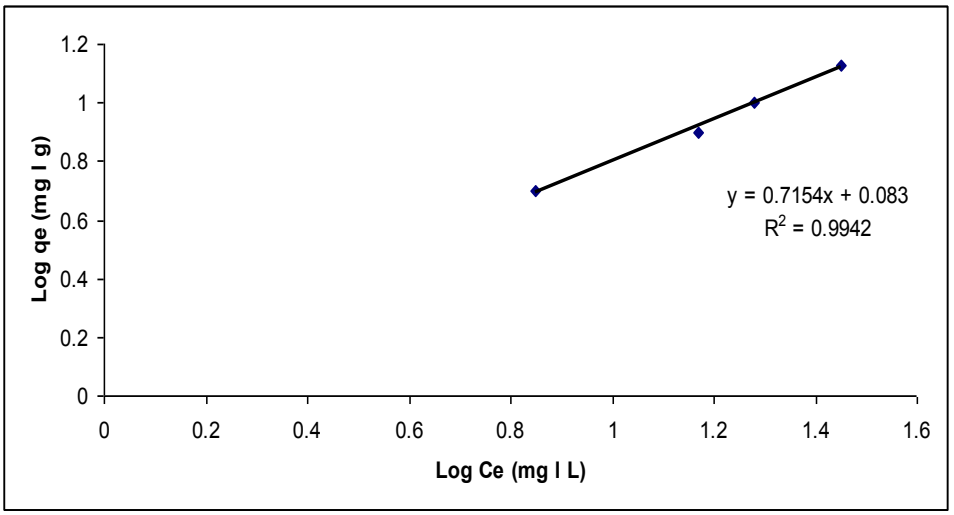


Figure (3.16) : Freundlich plot for DCF adsorption onto CTAC at (temperature: 25 °C, initial pH: 4 and solid/liquid ratio: 0.25 g/50 mL).

The adsorption isotherm parameters which were calculated from the slope and intercept of the linear plots using the linear zed form of the Langmuir and Freundlich equations, together with the R^2 values are given in Table (3.5) :

Table (3.5): Isotherms constants for DCF adsorption onto CTAC

Langmuir Isotherm			Freundlich Isotherm		
R^2	K_L (L/mg)	Q_{max} (mg/g)	R^2	K_F ((mg/g)(L/mg)$^{1/n}$)	N
0.952	0.0467	22.22	0.9942	1.211	1.398

It is clear from the R^2 values that the Freundlich isotherm is fitted to the experimental data more than Langmuir isotherm model. The Freundlich isotherm shows that adsorption will increase with increasing diclofenac sodium (DCF) concentration and this adsorption occurred in multilayer system rather one layer.

A favorable adsorption tends to have Freundlich constant (n) between 1 and 10. Larger value of n (smaller value of 1/n) implies stronger interaction between the adsorbent and the adsorbate. From Table 3.5 it can be seen that (n) value was between 1 and 10 showing favourable adsorption of diclofenac sodium (DCF) onto the activated carbon prepared from cyclamen tubers.

This finding validates that the assumption of multilayer physical adsorption between the adsorbate (DCF) and the adsorbent surface (CTAC) is achieved.

3.3.5.7. Kinetics of DCF Adsorption onto CTAC

The adsorption kinetics of DCF onto cyclamen tubers activated carbon (CTAC) was evaluated using the linearzed pseudo-first-order and pseudo-second-order equations, represented in the literature.

Adsorption kinetic of DCF onto CTAC at 25 ºC using pseudo-first-order adsorption model was given in Figure (3.17) .

Adsorption kinetic of DCF onto CTAC at 25 ºC using pseudo-second-order adsorption model was given in Figure (3.18) .

Intra-particle diffusion (Weber-Morris) kinetic model for DCF adsorption onto CTAC at 25 ºC was given in Figure (3.19) .

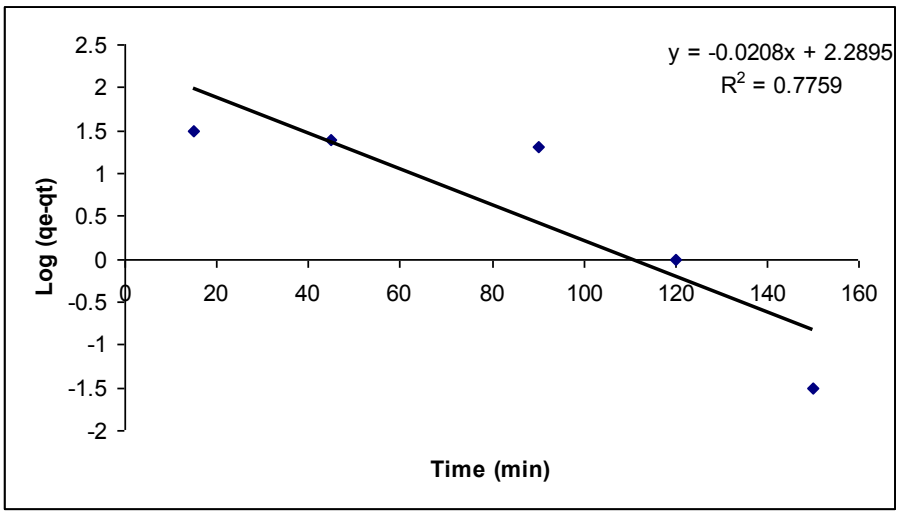


Fig (3.17): Pseudo-first order kinetic modeling of DCF adsorption onto CTAC

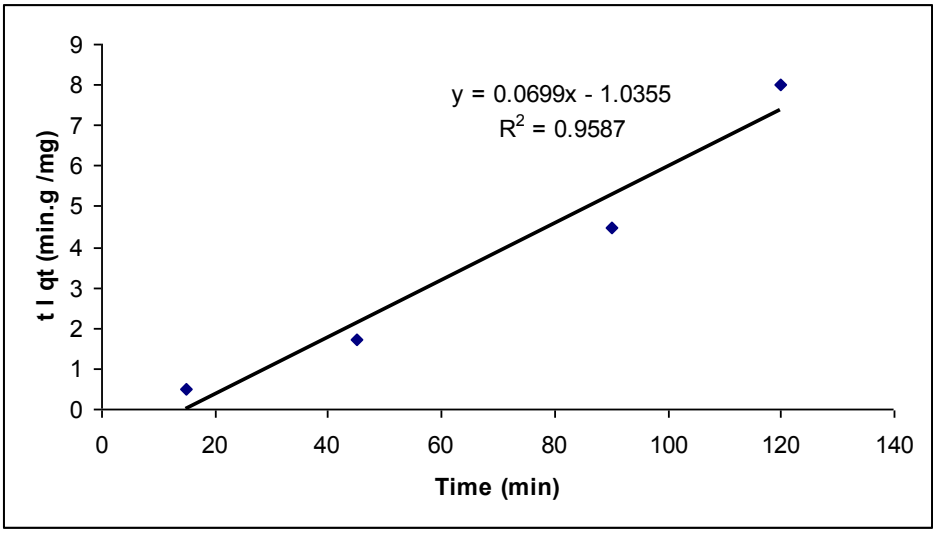


Fig (3.18): Pseudo-second order kinetics modeling of DCF adsorption onto CTAC

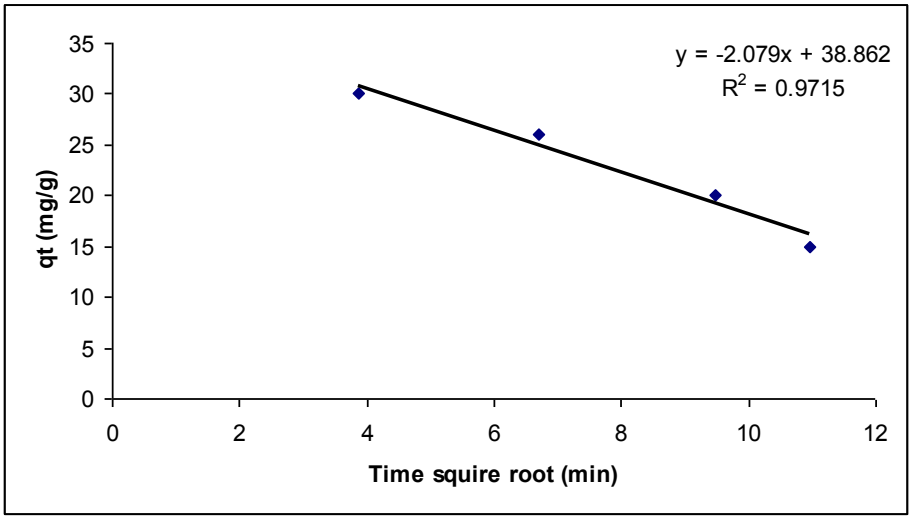


Fig (3.19): Intra-particle diffusion (Weber-Morris) modeling of DCF adsorption onto CTAC.

Kinetic adsorption models parameters of DCF adsorption onto CTAC were summarized in table (3.6) and (3.7):

Table (3.6) : Pseudo-first-order and pseudo-second-order kinetic model parameters for DCF adsorption onto CTAC at 25 ºC.

Pseudo-First Order		
k_1	q_e	R^2
min^{-1}	(mg/g)	
0.048	48.7	0.7759
Pseudo-Second Order		
k_2	q_e	R^2
(mg/(g.min))	(mg/g)	
211.9	14.31	0.9587

Table (3.7) : Intra-particle diffusion kinetic (Weber – Morris) model parameters for DCF adsorption onto CTAC at 25 ºC.

Weber-Morris	
K_b	R^2
$(mg/g.min^{-0.5})$	
2.079	0.9715

Reaction modeling of DCF adsorption presented in Fig (3.17), (3.18) indicated that physical adsorption plays an important role in DCF adsorption onto CTAC, taking into consideration that correlation coefficient (R^2) of the reaction models presented in Table (3.6) is close to unity for pseudo-second-order. So better representation of pseudo-second order kinetic is observed over pseudo-first order kinetic.

Intra-particle diffusion kinetic (Weber – Morris) model gave a positive intercept value and value of correlation coefficient near to unity so this

model could describe the adsorption process although the linear line not pass through origin point.

3.3.5.8. Thermodynamic of DCF adsorption onto CTAC

The thermodynamic parameters of the adsorption process for DCF onto activated carbon from cyclamen tubers including changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) of adsorption can be calculated by means of the following equations.[84]

$$\ln K = \frac{-\Delta H^\circ_{ads}}{RT} + \frac{\Delta S^\circ_{ads}}{R} \qquad (3.3)$$

where R is the universal gas constant (8.314 J.mol^{-1}.K^{-1}), and T is the absolute temperature, (K) is the distribution coefficient of the system which can be calculated as: $K = C_i/C_e$.

where C_i (mg) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration of DCF.

The variation of Gibbs free energy (ΔG°_{ads}) was estimated according to the following expression [87].

$$\Delta G^\circ ads = - RT \ln K \qquad (3.4)$$

The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear variation of ln K with reciprocal temperature (1/T) in Figure(3.20) . The obtained thermodynamic values are given in Table 3.8.

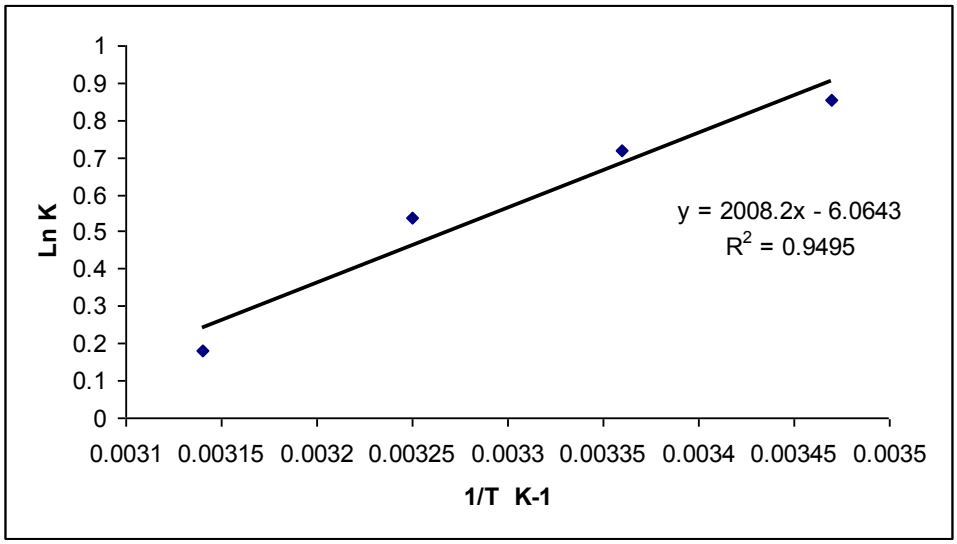


Figure (3.20) : Thermodynamic adsorption plot of ln K versus 1/T for 50mg/L DCF Concentration.

Table (3.8) : Thermodynamic parameters for DCF adsorption onto CTAC at different temperatures with initial concentration of DCF of 50 mg /L.

T (Kelven)	K	ΔH° (Kj/mole)	ΔG° (Kj/mole)	ΔS° (j /mole.k)
288 298 308 318	3.56 2.82 2.16 1.80	-17.45	-3.04 -2.55 -1.97 -1.55	-50.076

The increase in temperature caused a decrease in the amount of the pharmaceutical DCF that was adsorbed onto the activated carbon under equilibrium conditions. The decrease in adsorption capacity can be related

to two factors: the solubility of the pharmaceuticals in water and the energy exchange that occurred during the process.

Thus, the temperature increase possibly caused an increase in the solubility of the DCF, which hindered its adsorption because the pharmaceutical would have more affinity with the solvent than with the adsorbent. The force of the attraction between the DCF and the activated carbon decreased as a function of increasing temperature because the increasing temperature caused an increase in the agitation of the dissolved chemical species, reducing its physical interaction with the adsorbent. Moreover, the adsorption process was exothermic, which confirmed the decrease in adsorption capacity with increasing temperature because as heat is released to the system, the equilibrium shifted to the opposite direction of the reaction.

Additionally, the $\Delta H°$ was less than 40 kJ/mol, suggesting a physisorption process .Concerning the change in free energy, the adsorption process of the DCF onto CTAC was spontaneous, depending on temperature.

3.4.Conclusion

1. Activated carbon produced from cyclamen persicum tubers gave a good percentage of yield reaching 45% with highest adsorption capacity when activated by zinc chloride.

2. Optimum percent of DCF removal 82% when CTAC dosage 0.7g and DCF concentration 70mg/L and 77% for Eucarbon.

3. Percentage removal of DCF increases when the concentration of DCF increases with maximum percentage removal reaching 81% when DCF concentration was 70 mg /L and 0.25g CTAC.

4. At lowering pH from 6 to 2 the DCF adsorbing increases to reach its optimal value at pH 2, the decrease in DCF adsorbing was observed at pH from 7 to 12 .

5. The results showed that equilibrium time for DCF adsorption on CTAC is 120 min, and 150 min for Eucarbon ,but most adsorption attained within the first fifteen minutes for CTAC and within thirty minutes for Eucarbon.

6. DCF adsorption uptake increases when temperature is decreased indicating ionization of DCF at higher temperature and so decreasing its uptake by adsorbents surface.

7. The results showed that DCF adsorptions onto CTAC can be described by pseudo-second-order model, that resulted in correlation coefficient value near to unity.

8. Frenundlich equilibrium model describes the adsorption isotherm of DCF onto CTAC more efficiently than Langmuir model.

9. The values of thermodynamic parameters indicated that the adsorption process was spontaneous and exothermic one.

Recommendations for future researches.

This work has given a good accepting results, there are number of areas that need further investigation. These include:

1- Studying the adsorption efficiency of this prepared activated carbon for heavy metals and other pharmaceutical preparations.

2- Studying the effect of other pharmaceuticals in the aqueous medium on DCF adsorption.

3- More advanced characterizations for CTAC.

4- Studying chemical composition of the raw material using gravimetric analysis.

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جامعة النجاح الوطنية
كلية الدراسات العليا

استخدام الكربون المنشط والمستخلص من ابصال نبات قرن الغزال في ازالة دواء ا يكلوفن من محلول مائي

إعداد

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إشراف

ا . شحدة جودة

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قدمت هذه الاطروحة استكمالا لمتطلبات نيل درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين .

2013

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الملخص

تم اعداد ه ا البحث بهدف استخلاص مادة ذات تاثير مضاد للبكتيريا من ابصال نبات قرن الغزال ؛ ستخدام طريقة الغلي البسيط في مذيب الميثانول ، وتم الحصول على مستخلص ميثانولي جيد وصلت نسبته الـ (w/w)ذ 9 ، عند اختبار فاعليته كمضاد بكتيري اظهر قدرة عاليه ضد بكتيريا ***Staphylococcus. aureus*** . ومن ثم اعادة استخدام الانسجة المتبقية بعد غسلها جيدا بالماء قطر وتجفيفها بالفرن، لانتاج الكربون المنشط بعدة طرق مختلفة منها التنشيط الفيزيائي والتنشيط الكيميائي باستخدام حامض الفسفوريك وكلوريد الزنك ومحلول هيدروكسيد البوتاسيوم القاعدي ، وقد تم بعدها مقارنة العينات المحضرة لاختيار الافضل وذلك بدراسة مساحة السطح عن طريق الرقم اليودي الذي اظهر ان كلوريد الزنك انتج اعلى مساحة سطح للكربون النشط والتي وصلت الى (mg/g 06.78ذ). ولدى مقارنة التخطيط الطيفي للعينات بجها FTIR اظ ، ت النتائج ان حامض الفسفوريك قد حافظ على المجموعات الوظيفية الموج دة على سطح الكربون اكثر من غيره ؛ اما بالنسبة لتحليل العينات باستخدام جهر الا كتروني الماسح فقد تبين ان هيدروكسيد البوتاسيوم قد احدث ، ثر عدد من الفجوات المتاحة للادمصاص على سطح الكربون المنشط .

تم بعد ذلك استخدام هذا الكربون ، نشط في ازالة المستحضر الصيدلاني ديكلوفن الصوديوم بطريقة الادمصاص من محلول مائي، ومقارنة فاعليته مع عقار ®Eucarbon المتوفر في السوق علاج الحالات المتاحة لعملية الا مصاص كا سهال والغازا . وقد اظهرت النت ج ان

نسبة الازالة وصلت الى ٪ 2 باستخدام الكربون المنشط الذي تم تحضيره ، وقد تاثرت هذه النسبة كثيرا بدرجة حرارة ودرجة حموضة وتركيز الـ يكلوفين وكذلك جرعة المادة التي يحدث عليها الادمصاص . حيث زادت نسبة الازالة الى ٪ 81 على درجة حموضة تحت 6 وتركيز ديكلوفز 70mg/L ودرجة حرارة منخفضا 15 درجة مئوية وجرعة 0.7g للمادة التي ت م بالادمصاص .

اما بما تميز به الكربون الـ ي تم تحضيره عن عقار ®Eucarbon في عـ لية الازالة هو ان الكربون المنشط احتاج الى 15 قيقة لتحقيق نسبة ازالة عالية لمستحضر الديكلوفن بينما تتطلب ذلك 30 دقيقة باستخدام عقار ®Eucarbon .

تم استخدام معادلتي فرندليخ ولانجمير في دراسة الية الاتزان في ادمصاص الديكلوفن على الكربون المنشط لتظهر النتائج ان معادلة فرندلخ كـ ت افضل في وصف عملية الاتزان هذه بقيمة n equal to 1.398 ، وهذا يعزز كون عملية الادمصاص على السطح كانت فيزيائية .

وقد نجح نموذج الاعتماد من الدرجة الثانية ظاهريا ونموذج تدفق الدقائق إلى داخل الجسيمات في وصف طريقة الادمصاص ليعزز ذلك من كون العملية نتيجة تجاذب فيزيائي وليس كيميائي بين مستحضر الديكلوفن وسطح الكربون المنشط . وللتوصل الى ان هذا التجاذب كان من النوع الطارد للحرارة تم دراسة عوامل التفاعل الكيميائية مثل ΔH° و ΔG° ΔS° ليظهر من خلالها ان التفاعل طـ ارد للحرارة بقيمة ΔH° الاقل من $40\ kJ\ mol^{-1}$ وقيمة ΔG° السالبـ . وفي الختام، نسأل الله تعالى التوفيق والسداد في الدارين، والحمد لله رب العالمين .