

**An-Najah National University**

**Faculty of Graduate Studies**

**Comparative Study between Commercial  
Charcoal and *Asphodelus ramosus* Tuber  
Derived Activated Carbons for Adsorption  
of Heavy metals from Aqueous Solution**

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III

**Dedication**

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

To my brothers , my sisters 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.

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أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

**Comparative Study between Commercial Charcoal and  
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Adsorption of Heavy metals from Aqueous Solution**

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## List of Abbreviation

$C_e$	Equilibrium concentration of the adsorbate.
$C_i$	Initial solution concentration.
$K_L$	Langmuir constant.
$K_F$	Freundlich relative adsorption capacity constant.
$q_t$	Adsorption capacity at time $t$ .
$K^*$	Equilibrium constant of adsorption.
$C_0$	Initial solute concentration fed to fixed bed.
$C_t$	adsorbate concentration in the fluid phase at time $t$ .
<b>CAC</b>	Commercial Activated carbon.
<b>AAC</b>	<i>Asphodelus</i> Activated Carbon.
<b>IN</b>	iodine number (mg/g).
<b>PR</b>	percentage removal (%).
<b>q<sub>e</sub></b>	Amount of adsorbate per unit mass of adsorbent at equilibrium(min).
<b>q<sub>t</sub></b>	Amount of adsorbate per unit mass of adsorbent at time $t$ (min).
<b>R</b>	Correlation coefficient.
<b>V<sub>b</sub></b>	are volumes of sodium thiosulfate solution required for blank .
<b>V<sub>v</sub></b>	cylinder volume packed with dried activated carbon (ml).
<b>V<sub>s</sub></b>	are volumes of sodium thiosulfate solution required for sample titrations(mL) .
<b>Pb(II)</b>	Lead ion
<b>Cr (III)</b>	chromium ion
<b>Cu(II)</b>	copper ion
	cadmium ion

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**Abstract**

In this project *Asphodelus ramosus* Tuber was subjected to several in-vitro investigations to show its antioxidant, and anti-obesity using different solvents for extract preparation . Activated carbon was prepared from this tuber tissues by different methods then to set up kinetic study of some heavy metals adsorption from aqueous solution onto this activated carbon to evaluate the power of this plant tubers to environmental purification from these harmful heavy metals and compared it with commercial activated carbon.

The results of phytochemical screening tests showed that *Asphodelus ramosus* tuber methanolic extract was rich in phytochemical compounds like Flavonoid, glycosides, phenols, alkaloids, proteins, carbohydrates, tannin while antioxidant activity evaluated by using 2, 2-diphenyl-1-picrylhydrazyl-hydrate assay also showed that methanolic extract was the best one in its antioxidant activity with  $IC_{50}=13.8\mu\text{g/ml}$  which is close to  $IC_{50}=2.08\mu\text{g/ml}$  for Trolox ( the standard reference compound).So these tubers can be a good candidate of manufacturing biological and pharmacological active pharmaceuticals, cosmeceuticals and nutraceuticals formulations as it has good antioxidant effect. On the other hand anti lipase investigation

showed that the methanol extract had the least value of the half maximal inhibitory concentration  $IC_{50}$  which was 63.09 then aqueous extract with  $IC_{50}$  value =79.43, while higher values for  $IC_{50}$  were obtained for both acetone and n-hexane extracts which were 316 and 630 respectively. Comparing these results with orlistat  $IC_{50}$  which was 12.3 both acetone and n-hexane extracts seems to be not active as lipase enzyme inhibitors. while the methanol extract was the most potent one as natural anti-lipase inhibitor .

Adsorption capacity of AAC for heavy metals from aqueous solution was expressed using Freundlich and Langmuir models to study adsorption isotherm at equilibrium. In order to determine whether the adsorption process is chemical or physical, two kinetics models were used.

Results also showed that the activated carbon produced from *Asphodelus ramosus* tubers showed largest Surface area that determined by iodine number was 506.5mg/g using zinc chloride as activating agent.

Results showed that Percentage removal of all heavy metals Cr(III), Cu(II), pb(II) and Cd(II) increases with increasing in both temperature and pH value as optimum adsorption occur at 45°C and pH=12 .

The effect of heavy metal concentration on adsorption by CAC and AAC has also been investigated in the range of ( 5-80 ppm) . The results indicated that the best adsorption capacity occur at low concentration as when 5ppm was used the %Removal reach 99.7%, 92.9%, 91.1% and 57.06% for pb(II), Cr(III), Cu(II) and Cd(II) respectively.

The equilibrium adsorption time for all investigated heavy metals was 7hr for both *Asphodelus ramosus* tuber and commercial activated carbon, but most of the adsorption attained within the first 30 min

Freundlich model describe adsorption isotherm of all screened heavy metals more efficiently onto AAC with  $n$  ranging between 1 to 10 that indicated favorable adsorption. This finding validated the assumption of multilayer physical adsorption process of heavy metal ions on activated carbon.

## Chapter One

### General Introduction

#### 1.1. Research overview

Some of the plants are considered good sources of antioxidant substances, as they use these antioxidants for their own protection. An antioxidant can be broadly defined as any substance that delays or inhibits oxidative damage to a target molecule[1]. The main characteristic of an antioxidant is its ability to trap free radicals. Antioxidant compounds like phenolic acids, polyphenols and flavonoids scavenge free radicals such as peroxide, hydro peroxide or lipid proxy and thus inhibit the oxidative mechanisms that lead to degenerative diseases. Herbal plants are considered as good antioxidant since ancient times [2].

Obesity results from complex interactions of genetic, behavioral and environmental factors correlating with economic, social status and life styles . A considerable interest has recently aroused to the potential of natural products for their health promotion and disease prevention . Their action on multiple molecular targets, thus offers advantages over treatments with single chemicals. These products contain dietary phytochemicals with high potential anti-obesity effects are mediated by regulation of various pathways, including lipid absorption [3-4].

Medicinal plants possess immunomodulatory and antioxidant properties, leading to antibacterial activities. They are known to have versatile



immunomodulatory activity by stimulating both non-specific and specific immunity . In the last few years, a number of studies have been conducted in different countries to prove such efficiency. Many plants have been used because of their antimicrobial traits, which are due to compounds synthesized in the secondary metabolism of the plant[5].

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel [6].

In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair[7].

In this research we focused on copper, chromium, lead and cadmium heavy metals which have many sources and health impact for example ; Sources for polluted copper are: Copper Water pipes; Copper water heaters;; Frozen greens and canned greens using copper to produce an ultra green color, alcoholic beverages from copper brewery equipment; Instant gas hot water heaters; Hormone pills; Pesticides. insecticides; fungicides; Copper jewelry; Copper toxicity can be signed by; Anaemia, rheumatoid arthritis; Hypertension, Nausea/vomiting, Hyperactivity, Schizophrenia, Insomnia, Autism, Stuttering, Postpartum psychosis,

Inflammation and enlargement of liver, heart problem, Cystic fibrosis[8].

Activated carbon has shown to be an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. Because of its high surface areas that range from 500 to 1500 m<sup>2</sup> it is widely used in the treatment of wastewaters. The effectiveness of Activated carbon in cleaning up polluted water is due to its well developed porosity structure as well as the presence of a wide spectrum of surface functional groups. This makes it capable of distributing pollutants on its large internal surface, making them accessible to reactants . Effectiveness of activated carbons to act as adsorbents for a wide range of contaminants is well noted [9-10].

Developing activated carbon for medicinal purposes focuses on herbal resources as precursors of the carbon material such as vegetable residues, coconut-shell, palm seeds, olive stones, mixture of apricot and peach stones, rice husks etc... while 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[11].

## **1.2. Hypothesis of this work**

This work based on a hypothesis that *Asphodelus ramosus* tuber will have considerable health benefits when its different extracts are investigated in-

vitro on free radical scavenging power to evaluate antioxidant activity ,biological effect on several bacterial strains and as anti-obesity agent if tuber extracts act as inhibitors on lipase enzyme.

Also *Asphodelus ramosus* tuber may form an efficient natural source for developing herbal activated carbon with high capacity for adsorption of various toxic materials especially heavy like chromium, lead, cadmium and copper which have toxic effect on both environment and human life.

### **1.3. Objectives**

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

- Preparation of different extracts from tubers using solvents with different polarities like n-hexane, acetone, methanol and distilled water.
- In-vitro antioxidant, anti-obesity investigation of these different tuber extracts .
- Production and characterization of activated carbon from the tissues of tubers.
- Study the effect of chemical activation on the development of pore structure of the produced activated carbon.
- Study adsorption isotherms, kinetics of some heavy metals adsorption onto activated carbon produced from these tubers.
- Compare the adsorption capacity of this prepared activated carbon with commercial activated carbon.

#### 1.4. Methodology

This scientific research focused on making tubers a good medical source for biological applications, this is will be achieved by the following steps; preparing different types of tuber extracts using several solvents for extraction, this extract was evaluated in-vitro to screen its biologic effect as antioxidant, anti-obesity and antibacterial effects

Also in this research aimed to develop a good natural source for activated carbon production from this *Asphodelus ramosus* tuber by using chemical impregnation and physical activation. For production of activated carbon by physical process, the tissues obtained from tubers were subjected to carbonization and then activation under nitrogen gas in single thermal decomposition step.

While chemical impregnation with certain activating agents was carried out in chemical activation process before carbonization. Two chemical activating agents were used, zinc chloride and potassium hydroxide, in using zinc chloride as activator we focused on modification of pores structures by the chemical dehydration effect of zinc chloride as its Lewis acid. but for 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 [12].

## Chapter Tow

### **In-vitro investigation of phytochemical contents, antioxidant, anti obesity of *Asphodelus ramosus* tuber different extracts**

#### **2.1. General background**

*Asphodelus ramosus* L. (Asphodelaceae) is a perennial geophyte, its characterized by roots having napiform shape. The leaves of this medicinal plant have flat, somewhat keeled. The lateral branches appear as long as terminal ones . the origin of this medicinal plant is southern Europe especially southern parts , northern regions of Africa, and some parts on Middle East. Canary Islands are also can be a natural source for this plant [13-14].



**Figure (2. 1) :** *Asphodelus ramosus* plant parts

In the subterranean tissues (tubers) of *Asphodelus ramosus*, C-glycosylflavones [19], 7'-[chrysophanol-4-yl]--chrysophanol-10'--anthrone 10'-c-glycosides [20], (-)--10'-C-[ $\beta$ -d-gluco-pyranosyl]-1,1',8,8',10,10'--hexa-hydroxy-3,3'-di-methyl-10,7'-bi-anthracene-9,9'-di-one [21], (-)-10'-C-[ $\beta$ -D-xylopyranosyl]-and(-)10'-c-[ $\beta$ -D-glucopyranosyl-(1,4)- $\beta$ -D-glucopyranosyl]--1,1',8,8',10,10'--hexa-hydroxy-3,3'-dimethyl-10,7'-bi-anthracene-9,9'-dione, also 10'-deoxy-10-epi-ramosin [22] were isolated and identified.

### **2.1.1. Qualitative phytochemical screening tests for identification of active therapeutic compounds in the extracts:**

It was found that some medicinal plants may have some effects as healing and managing of human diseases due to their content of some phytochemical active compounds. [19]. Compounds named as Phytochemicals are naturally occurring in different medicinal plant parts like leaves, stem bark, fruits also other parts like Roots that acts as a role in defending and protecting mechanisms from various diseases for any plant system. These Natural products obtained from plants called usually as secondary metabolites which are the end products of primary metabolites like carbohydrates, amino acid, and chlorophyll lipid .

So these precursor compounds are used later for synthesis of large variety of chemical substances known as secondary metabolites which include alkaloids, flavonoids, glycoside, saponin compounds , steroids, tannins, , terpenoids and phenolic compounds [20]. For phytochemical

investigation we usually need to identify and perform isolation of these active compounds to make it more effective in the known therapeutic application. It will lead to better understanding of diseases if The present consumes from taking certain plants that have no medicinal value or poisonous will known [21].

### **2.1.2. Antioxidant activity investigation using free radical scavenging power:**

For in- vitro investigation of antioxidant activity these antioxidant can be defined as compounds which delay or may stop the damage initiated from free radicals as they give electrons to these damaged cells. Commonly these compounds will alternate free radicals into by-products, which are eliminated from human bodies. It was found that focusing on antioxidant-enriched fruits and vegetables in the daily diet is known to lower the dangerous diseases initiated by free radicals that may present. About this healthy benefit of fruits and vegetables may be due to the presence of complex poly-phenols, carotene derivatives, and vitamins like E- and C- which are natural products presents in these plant sources [22-23]. Despite it was found that these phenol containing compounds are usually found in edible and also in non-edible herbs, cereal products, fruits, also vegetables, oils, spices are now of certain interest, and other plant sources [24-25], scientific overview on the antioxidant properties of endemic plants is usually scare because the availability of these certain endemic plants is limited to regions presented in and this will affect the environmental availability for

these endemic limited plants, consequently it seemed to be important that assessment of such properties must be always of special focus and should be of useful task, to develop promising--sources for natural antioxidants to be used functional foods as well as in nutraceuticals [25-26].

In the past few decades, there were huge advancements in the utilization of medicinal natural products in Europe, America, as well as people all over the world. This articulated a considerable interest and even an increased preference for their pharmaceutical forms and many names were given to these products such as botanical medicines, folkloric medicines, herbal medicinal products, herbal remedies, herbal medicines and traditional medicines[27].

### **2.1.3. Anti-obesity evaluation using lipase inhibition assay:**

It was reported in 2010 that overweight as well as obesity is 2.8 millions claiming lives annually . these data was mentioned by World-Health - Organization (WHO) also it was appeared that plague of deal of Obesity has become epidemic proportions and is widely spreading at an unprecedented pace, especially in the urban regions with low also in middle income countries [28-30].

Among the most used herbals and phytopharmaceuticals these which utilized for treatment of overweight and obesity because these metabolic disorders became very popular especially in the developing and developed countries [31-32].



Obesity was reported to be associated with many health problems such as endocrine, metabolic and cardiovascular disorders. It is well known that various therapeutic protocols utilized globally to control excess body weights and hyperlipidemia in obese patients. In fact, many of drugs are recently available in the pharmaceutical markets globally and used for this purpose, which recommended to use hand to hand with the required diet and exercises for reduction of body weight and decreasing the levels of lipids in the plasma [33-35].

In this project Pancreatic lipase assay was adopted as this enzyme is the main enzyme for fats and lipid materials digestion, the mechanism of action for lipase is in removing of fatty-acids presents on triglyceride compounds, that produce  $\beta$ -monoglyceride which is lipolytic product and long chain saturated and poly-unsaturated fatty acids. So to inhibit this enzyme it become an attractive targeted approach for developing of potent anti-obesity agents for controlling of Obesity problem [36-37].

In screening for the developing of anti-Obesity medications from adopted methods is to find potent lipase enzyme inhibitors from medicinal herbal extract. Medicinal herbs have been traditionally consumed as natural medicines for developing healing of different diseases and various are reported to have biological effects and activity [38].

## **2.2. Experimental set up**

### **2.2.1. Materials and methodology**

#### **2.2.1.1. Plant material**

*Asphodelus ramosus* tubers were collected from different sites in Jenin and Nablus cities between the months of July and September, 2016. The tubers were dried in shade for two weeks, then grounded using electronic grinder to obtain powdered tubers.

#### **2.2.1.2. Chemical reagents for phytochemical analysis:**

**Simple laboratory** phytochemical screening tests were performed to identify active compounds in the different extracts for these tests we used reagents like: Millon and Benedict's reagents were from Gadot-- Israel, Nin-hydrin solution (Alfa Agar -- England), Molish's reagent, H<sub>2</sub>SO<sub>4</sub> and Iodine solution were obtained from England company of Alfa-Aesar, while NaOH, Chloroform, and HCl were purchased from Germany company of Sigma Aldrich,, Magnesium ribbon, Acetic acid (Frutarom LTD, Israel), FeCl<sub>3</sub> (Riedeldehan, Germany). Folin-Ciocalteu's reagent (Sigma Aldrich, Germany) .

For Porcine lipase inhibition assay the used chemicals were: Dimethyl sulfoxide, p-nitrophenyl butyrate, Orlistat, and tris-HCl buffer, were purchased from Sigma-Aldrich (Germany), while from Sigma( USA) we

purchased Porcine pancreatic lipase type II, and from SPF (India) we purchased acetonitrile

For antioxidant—evaluation reagents needed were: Methanol obtained from India company of Lobachemie, while n-hexane was from Israel company of Frutarom LTD, the reference compound Trolox—[(s)-(-)-6 hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid] was (Sigma-Aldrich, Denmark), and DPPH--[2,2-Diphenyl-1-picrylhydrazyl] (Sigma Aldrich, Germany).

#### **2.2.1.3. Instrumentation**

For drying organic extract we used rotary--evaporating device [Germany -Heidolph OB2000] while for drying aqueous extract we used freeze dryer (Mill rock technology, model BT85, Danfoss, China), also grinder for milling dried tubers, balance (Radwag, AS 220/c/2, Poland) also was used, finally filter papers (Macherey-Nagel, MN).

#### **2.2.1.4. preparation of different extracts from *Asphodelus ramosus* tubers**

The dried powder of *Asphodelus ramosus* tuber was extracted by adding solvents with variable polarities: hexane--acetone--methanol and water. About 100 grams from the dried and grounded tubers were soaked in 1L of four different solvents (water, methanol, acetone, n-hexane) separately and placed each one in a shaker device at 100 rounds per minute for 72 hours at 25°C, and then stored in refrigerator for 4 days. After that, each

organic extract was filtered and concentrated under vacuum using rotary evaporator. While aqueous extract was dried using freeze dryer. Finally all produced extracts were kept cautiously at 4 °C [39].

#### **2.2.1.5. In-vitro qualitative phytochemical screening tests:**

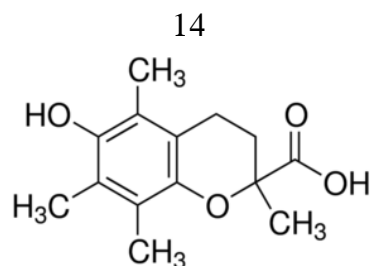
Several simple laboratory qualitative phytochemical tests were performed for the identification of primary and secondary metabolic compounds which were mentioned in our literature especially flavonoidal compounds, proteins, starch, aromatic oils, phenol group containing compounds, glycosides, saponins, phyto--steroids, and finally tannins [40].

#### **2.2.1.6. Free radical scavenging assay for Antioxidant activity:**

The following protocol for in—vitro antioxidant assessment for our extracts from Tubers was adopted. plant were measured by [1, 1- diphenyl-2-picrylhydrazyl] abbreviated by DPPH according to following procedure[41]:

- **Experimental steps For preparation of standard reference and tuber extracts testing solutions:**

100 mg of tuber extract was dissolved in 100mL methanol to prepare stock solution was prepared for plant extract and Trolox (standard reference compound). From this Stock solution serial dilutions were prepared .Several serial dilutions were prepared and ranging between (1 µg/ml to 80 µg/ml) for the construction of %DPPH inhibition curve.



**Figure (2. 2) : Trolox structure**

- **Data analysis by using Spectrophotometer :**

Spectrophotometric method was adopted for in-vitro antioxidant evaluation as a solution of DPPH( free radical compound) which was prepared immediately by dissolving of 2mg of DPPH compound in 100mL of methanol as solvent. The blank which was used as the first tested sample was consists of DPPH mixing with methanol only . All test tubes were left at room temperature in a dark place for about 30 minutes. Then, their optical densities values were obtained at 517nm as this is a wave length at which DPPH has maximum absorption value.

**Percentage of inhibition of DPPH by plant different extracts and Trolox:**

the following Rule was adopted in our calculation for evaluation of free radical inhibition

$$\text{DPPH inhibition activity (\%)} = (Y-S)/Y \times 100\%$$

Where Y is the measured absorbance of our--blank and S is for our -- sample absorbance that containing tuber extract.

**2.2.1.7. Pancreatic Lipase Inhibition assay for anti-obesity evaluation:**

The porcine pancreatic lipase inhibitory assay with some modifications [42]. Prepared 1mg/ml (1000mg/mililiter) *Asphodelus ramosus* extract

stock solution in [10% dimethylsulfoxide ] from which diluted solutions were prepared with the following concentrations (50, 100, 200, 300, 400 µg/ml). While 1mg/ml stock solution of pancreatic lipase enzyme was prepared immediately before use was suspended in tris-HCl buffer. This procedure was carried out for the twelve plants species.

Stock solution of PNPB (p-nitrophenyl butyrate) was prepared by dissolving 20.9 mg in 2 ml of acetonitrile. For each working test tube, 0.1ml of porcine pancreatic lipase (1 mg/ml) was added to a test-tube containing 0.2ml from each diluted test-tubes containing (50, 100, 200, 300, 400 µg/ml) plant extract.

The resulting mixture was then made up to 1ml by adding Tri-HCL solution and incubated at 37°C for 15 minutes. After the incubation period, 0.1ml of PNPB (p-nitrophenyl butyrate) solution was then added to each test-tube. The mixture was again incubated for 30 min at 37°C. Pancreatic lipase activity was determined by measuring the hydrolysis of p-nitrophenolate to p-nitrophenol at 405 nm using UV-visible spectrophotometer. The same procedure was repeated for aqueous, organic extracts and for Orlistat which was used as a positive control.

## **2.3. Results and discussion**

### **2.3.1. Phytochemical screening tests for *Asphodelus ramosus* different extracts**

The results for phytochemical analysis by the mentioned tests in lab of different extracts are summarized in (Table 1.1).after application of all mentioned qualitative phytochemical screening tests it was observed that

These bioactive compounds present in highest amount in the methanolic especially Flavonoid, glycosides, phenols, alkaloids, proteins, carbohydrates, tannin.

**Table(2. 1): Phytochemical screening tests for different extracts *Asphodelus ramosus***

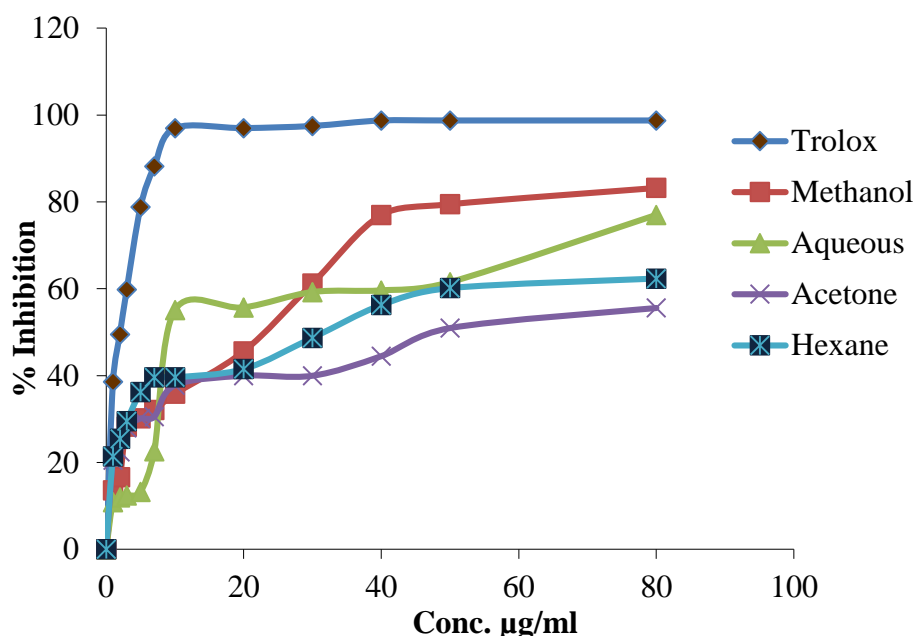
Phytochemical compounds	Test name	hexane	acetone	methanol	aqueous
<b>Protein</b>	Ninhydrin	-	-	+	+
<b>Carbohydrate &amp; reducing sugars</b>	Fehling	-	-	+	+
	Benedicts	-	-	+	+
	Molisch	-	-	+	+
	Iodine	-	-	+	+
<b>Glycoside</b>	Liebermants	-	+	+	+
	Keller-kilani	-	+	+	+
<b>Flavonoid</b>	Shinoda	-	+	+	-
<b>Saponin</b>	Frothing	-	-	-	-
<b>Phytosteroids</b>	Liebermann	+	-	-	-
<b>Volatile oil</b>	KOH	-	-	-	-
<b>Phenols</b>	Folin- ciocalteu	+	+	+	+
<b>Tannin</b>	Ferric chloride	-	-	+	-
<b>Alkaloids</b>	Wagner's	-	+	+	-

### 2.3.2. Free radical scavenging assay for antioxidant evaluation:

*Asphodelus ramosus* tuber results for DPPH inhibition were shown in figure (2.2) in the half maximal inhibitory concentration ( $IC_{50}$ ) was 13.8 $\mu$ g/ml for *methanol extract* and 2.08 $\mu$ g /ml for Trolox.

While other extract showed weak antioxidant activity with higher ( $IC_{50}$ ) value which was 19.05 $\mu$ g/ml for aqueous , 24.54 $\mu$ g/ml for hexane and 52.48 $\mu$ g/ml for acetone extract. from these values methanol extract seemed to be the best one as antioxidant agent this may be due to high content of

phytochemicals like phenols, alkaloids, Flavonoid and glycoside compounds in this extract.



**Figure (2. 3) :** DPPH Inhibition activity of Trolox standard and *Asphodelus ramosus* different extracts.

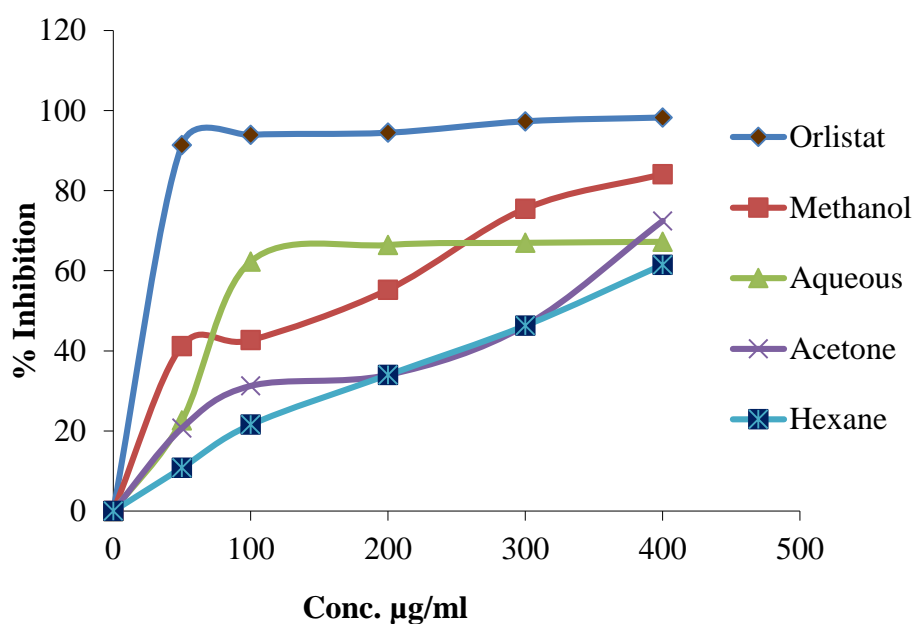
### 2.3.3. Porcine lipase inhibition assay for anti-obesity investigation:

The activity for different plant extracts as natural lipase inhibitors was shown in figure (2.3) compared with the activity of the reference compound orlistat which acts as potent inhibitor for lipase enzyme. Throughout the investigated results, the methanol extract show the least value of the half maximal inhibitory concentration  $IC_{50}$  which was 63.09 then aqueous extract with  $IC_{50}$  value = 79.43, while higher values for  $IC_{50}$  were obtained for both acetone and n-hexane extracts which were 316 and 630 respectively. Comparing these results with orlistat  $IC_{50}$  which was 12.3 both acetone and n-hexane extracts seems to be in active as lipase enzyme inhibitors.



The methanol extract was the most potent one as natural anti-lipase inhibitor and so may the best choice in the future to prepare anti-obesity formulations .

The results were shown figure (2.3).



**Fig (2. 4) :** The inhibitory effect of four different extracts of *Asphodelus ramosus tuber* and Orlistat on the activity of porcine pancreatic lipase.

## 2.4. Conclusion

The plant methanolic extract was rich in several phytochemical active ingredients like Flavonoid, tannins , phenols , Glycosides , proteins ,carbohydrates and alkaloids and this extract was the best one as antioxidant , anti-lipase agent. From these in-vitro investigations *Asphodelus ramosus* tubers can be an excellent choice for further pharmacological, clinical and phytochemical studies .

## Chapter Three

### **Activated carbon from *Asphodelus ramosus* Tubers for heavy metals removal from aqueous solution**

#### **3.1. General background**

The simplest identification of activated carbon as it is a substance that can be different from elemental simple carbon by the oxidation of the carbon atoms presented on the internal and external surfaces of the precursor we used [43]. Several agricultural by-products and wastes can be cellulose source precursor for the production of activated carbon also tough wood and bit-uminous coal. For example for these pre-course are sells of coconut and wood of Trees. During oxidation wet based methods reaction between the carbon surface and the prepared oxidizing chemical solution like strong acids as phosphoric acid ( $\text{H}_3\text{PO}_4$ ), nitric acid ( $\text{HNO}_3$ ), also a compound called hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) seems to be good oxidizing chemical, many researches also uses zinc compounds especially Zinc-chloride, permanganate salt ( $\text{KMnO}_4$ ), ammonium--per sulfate ( $(\text{NH}_4)_2\text{SO}_8$ ), potassium hydroxide ( $\text{KOH}$ ) as oxidizing agents for wet based oxidation methods[44].

It was reported in many researches that chemical activation of the sewage sludge with Zinc—chlride and sulfuric acid was good choice for establishing activated--carbon of high adsorption ability comparing with that type available commercially. On the other hand, a cheap raw

material for the establishing of activated carbon was chosen this means both significant savings availability in the establishing cost and a way recycling in waste material, so this reduces its disposal problems in the environmental field [45].

### **3.1.1. General methods for activated carbon production:**

- **Activation process are discussed in detail as following:**

Usually the adopted process in utilization of activated carbon is based on the nature of carbonaceous precursor material and nature of activating conditions. So this process may be achieved physically ; involving two steps the first is carbon producing process of the precursor material followed by gasification—controlled step (rate of heating, flowing of steam and Temperature ) ; the other way for activated carbon production is chemically, this process involved that the precursor raw tissues is macerated in a chemical compound and then heated to a temperature ranging between 450--700°C [46].

- **Physical activation process**

Here in this method the precursor material should be with less than 25% moisture, and then carbonized first at temperature ranging between 400 - 500 °C so the volatile matter will be removed and followed by subjecting carbon to selected oxidizing gases mainly used one is carbon dioxide or the ordinary steam in temperature range (800-1000 °C) with air in lower Temperature, in selective type of oxidation. The oxidation is preceded mainly by a primarily step

carbon producing process of raw material. In pyrolysis process of wood temperature usually starts on nearly 225 °C .

atmospheric oxygen is usually used for Carbon oxidation and exposing for CO<sub>2</sub> after that, consequently air must be excluded or highly controlled during carbonization and activation process. Thermal based treatment at high temperatures for activation of charcoal should be performed in (800--1000 °C ) range , consequently these in-complete combustion products burn up and then volatilize [47].

- **Chemical activation**

Two important advantages were recorded for Chemical activation which were that lignocelluloses material is particularly used as precursor, the first is when lower temperature used in the preparation is accomplished making preparation more economical comparing this process with physical activation. Another advantage is the percentage yield of chemically activated charcoal is usually higher for some degree comparing to the physical process in production of activated charcoal[48].

### **3.1.2. Environmental applications of activated based charcoal:**

For the environmental field it is usually appeared in gaseous--purification, metal extraction, purification process for gold and water, sewage or waste water-- treatment, air--filters presented in respirators as well as in gas

masks, and several other applications will be appeared for activated carbon [49].

Metal finishing is one of industrial usage of AC. Also in purification of electroplating solutions activated carbon will be the best choice. As it is main purification technical agent used for eliminating impurities like organic type ones from nickel bright--plating produced solutions. Several chemicals of organic type are added to plating based solutions for improving quality like depositing ability. Also to develop properties for example bright quality, smooth property and also ductility. Because of the flawing of current directly and electrolytic--reactions of anode based oxidation and cathode based reduction, additives especially of organic type generate un-wanted breaking down products in the obtained solution. [50].

### **3.1.3. Activated carbon medical applications:**

In the medicinal field Activated charcoal is usually used as antidote for the large number of poisons. The use of activated charcoal to treat poisonings has been known as early as 1830 by the French chemist bertrand. This process is usually produced through the pyrolysis of materials that contain carbon and it is mainly activated through oxidation process using high temperature steam. Activated charcoal has a large surface area which reaches about 1000 m<sup>2</sup>/g and has the capacity of adsorbing many types of drugs [51].

Cloths of activated carbon have gained increasing interest in recent years since they give comparative suitable advantages comparing with traditional models and potentialities for innovation in technology of different fields, one of these advantages ;ability to be used in cell therapy, like supporting growth of stem cell, main advantages arise from the small diameter of the fibers constituting ACC [52].

#### **3.1.4. Commercial available forms of activated carbon:**

In recent years commercially available forms of activated carbon are: powders, granular chips in various size ranges, and shaped or molded products extruded into rod-like shapes, which has diameter ranges between 0.8 to 6 mm and 3 to 10 mm in length. Production for commercial type is present as powdered form (P-AC), fiber shaped form (F-AC), or granular form (G-AC) according to application purposes . BET specific surface regularly performed values range of 500 up to 2000 m<sup>2</sup>/ gram for these forms of activated charcoal. Nowadays "super-activated carbons" is available and exhibit surfaces areas more than 3000 m<sup>2</sup>/ g. also its necessary to tell about macro-pore, meso-pore , in addition to micro-pore size that presented in a range 0.5--2.5 m<sup>2</sup> /gram [53].

#### **3.1.5. Identification methods for Surface characteristics and chemistry of activated carbon**

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):**

Direct observation of the changes in the surface microstructures of the carbons can be determined by using SEM analysis method, due to the modifications. The reaction of electrons and the specimen make a series of reaction steps to be initiated in a sample resulting in the production of signals having a property of gaining information related to an investigated specimen. Four major steps in SEM imaging process are involved. The first making sample ready, the scanning of specimen, preparation of image and image analyzing step[54].

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

A relative indicator of porosity in an activated carbon is an assay called iodine number. As it does not important to provide accurate measurement of the carbon's ability to absorb other species but Iodine number may be used as an approximation of surface area for some types of activated carbons, despite that it must be realized that any relationship between surface area and iodine number cannot be generalized. It varies with changes in carbon raw material,

processing conditions, and pore volume distribution . It is important to know that the presence of adsorbed volatiles, sulfur; and water may affect the results in measuring iodine number of an activated carbon. Iodine Number is considered as the most fundamental parameter can performed to characterize activated carbon performance. It gives an indication of the activity level (higher number indicates higher degree of activation) [55].

Micro pore ( $0 - 20 \text{ \AA}$ ) content in the activated carbon can be indicated using iodine number method ,the needed reagents in the application of iodine value in the laboratory are listed below:

- The first solution is 0.1N of the Iodine that should be prepared by dissolving 12.7 g iodine in 1 Liter of the Distilled water .
- 0.05Normality Sodium--thiosulfate pentahydrate solution [12.5 gram  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 liter DW)
- Also an 1% Starch solution as the used indicator should be freshly prepared
- Activated carbon that we intended to test its surface area

Experimental steps:

### **( I ) Standardization of Iodine solution**

From 0.1N Iodine solution 10 ml was pipetted in a volumetric conical flask, then about 2-3 drops of Starch freshly prepared solution was added. It should be noticed that The pale yellow color of Iodine Solution became Blue. carried out then titration by using 0.05 N



Sodium--thiosulfate till it becomes colorless. take the Burette reading that was taken is corresponding to blank reading.(B')

**'Activated carbon testing:**

0.2 gram of AAC was weighted then placed into the Iodine dry flask , after that from 0.1N Iodine--solution 40cc was added. shaking the flask well about 4 minutes and filtered. The filtrate was placed in a well dried flask and add 10cc of the filtrate to be titrated versus standard Sodium--thiosulfate solution making starch its indicator. consider Burette reading corresponding to (A')

Calculate as following :

Iodine number :  $C' \times \text{Conversion factor; mg/g}$

Factor:  $\frac{\text{Molecular weight. of iodine (127)} \times \text{iodine--normality} \times 10}{\text{Weight. of carbon} \times \text{Blank volume}(B')}$

$C' = B' - A'$

### **3.1.6. Heavy metals overview**

Heavy metals like (Cadmium, Nickel, Lead and Chromium) which are Earth's crust natural components that are usually associated with environmental toxicity. even at trace concentrations exposing to heavy metals is known to be harmful for our bodies in many exposure cases . The presence of these heavy metals in the environmental aqueous regions has a potentially damaging results on physiological--tissues and biological organs when their amount are higher the acceptable values . Because many heavy metals cannot be degraded or destroyed their toxicity could be

formed, from contaminated drinking-water (like pipes made from lead), increased ambient air concentrations near sources of emission, or ingestion via the food chain [56]. In recent years the increasing use of heavy metals in industry has resulted in high availability of metallic substances in natural water sources. Nowadays several technologies like adsorption, precipitation, membrane filtration, and ion-exchange that adopted to eliminate metal pollutants from water contaminated sources [57]. However, adsorption has proven to be economical and efficient used method for removing heavy metals, organic pollutants and dyes from polluted waters. Several adsorbents such as activated carbon, silica, and graphene can be also used in the purification of water contaminated by these heavy metals [58].

#### **3.1.6.1. Environmental impact of usually present heavy metals:**

The recent challenge environmentally is due to globalization and the fast increasing in industrialization which becoming more and more nuisance in human being. So it is important issue to develop an efficient and effective methods especially for chemical industries to control this pollution. Trace levels presented in sewage and effluents coming from industry but it was considered as major issue in environment concerned pollution. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. As we mentioned above heavy metals are available in environmental field as : Selenium, , Manganese, Aluminum, Mercury, Chromium ,Silver,, Iron, Copper Nickel, Tin, Molybdenum,

Lead. These heavy metals formed a serious threats to the human beings ,fauna and flora in the receiving water bodies[59].

Aquatic environment contains Chromium which exists mainly as two ionic forms : Trivalent and Tetravalent chromium Usually tetravalent is more harmful on human related physiological systems may precipitated in the food--chain then resulted in bad and harmful effects ranging from ordinary irritation of skin and may lead to cause carcinoma of lung in human beings[60].

### **3.1.6.2. Scientific methods for heavy metals removal from aqueous solution**

It becomes an important issue to purify inorganic--effluent from Heavy metals this can be achieved by variety of treatment applications. Also heavy metals removal from industrial wastewaters can be accomplished by using many treatment options, these options included unit operations as chemical precipitation, solvent extraction, complexation, coagulation, activated carbon adsorption, ion exchange, electro-deposition, cementation, membrane operations and foam flotation. Chemical precipitations, conventional adsorption. Among these methods precipitation is most economical and hence widely used, but many industries still use chemical procedures for treatment of effluents due to economic factors [61].

Recently Bio sorption is a developed procedure which established to purify contaminated water from heavy metals. also a process called Sorption is making ions to be transferred from phase of solution into

phase of solid, it really a set of processes, including reactions of adsorption as well as precipitation in the treatment technique. It is obvious that adsorption became an alternatively chosen as methods for waste-water treatment. As known adsorption is a mass transfer technique and bounded substances through physical or may be by chemical attractions surface of solid [62].

Water-soluble polymeric legends were added to Polymer-supported ultrafiltration (PSU) technique to interact with metal ions and form macro-molecular complexation by forming effluents from free-targeted metal ions. Advantages of the PSU named technology are the low-energy requirements involved in ultra-filtration, the very fast reaction kinetics and higher selectivity of separation of selective bonding agents in aqueous solution [63].

### **3.1.7. Definition of adsorption Process by activated carbon**

Adsorption process was the promising method for this purpose. For achieving a long term treatment as well as economically proven purpose. In case of heavy metals these toxic metals can be removed and minimized even at a low concentration by using adsorption process. Scientifically the application of adsorption as one practical treatment should be enhanced. High-quality effluent treatment models also economically to offer flexible designing and operating process is tended by adsorption process. Because of adsorption has sometime reversible characteristic used can be regenerated by suitable desorption process [64].

As activated carbon is very inexpensive locally and naturally available material can be efficiently performed for the eliminating of  $\text{Cd}^{2+}$  and so adsorption is most effective and economic method. Design flexibility and operating, and in several cases adsorption process will produce a good-quality in treating effluent. It is considered also that adsorption is sometimes reversible, by regenerating the adsorbents by a suitable chosen of desorption process[65]

#### **3.1.7.1. Adsorption isotherms**

in the process of adsorption for heavy metal into adsorbents several factors will affect this process like pH exten, adsorbent grams dosing, initial concentration, time for contacting i as well as temperatures [66].

One of the main points to determine the capacity uptake of heavy metals by adsorbents is the dose of adsorbent. As usually observed, the increase in the dose of adsorbents will increase in the adsorption capacity until reaching a limit. But if more increase in the dose, the adsorption capacity will be constant. adsorbent loading from 0.5 g until 2.0 g for removal of copper increase with increase of adsorbent loading this was studied by Wang [67]. Also the initial concentration will affect adsorption process as adsorption dosage gain a strong effect with the initial concentration of heavy metals. In general adsorption capacity increased with the increasing in the initial concentration of heavy metals. It had been shown also that initial concentration influence in overcome all mass transfer resistance between solid and aqueous phases. In many studies it had been shown that

the removal efficiency of heavy metal is concentration dependent and there exist decreasing trend if further increase initial concentration [68]. The interaction of functional group between the solution and the surface of adsorbent result in the adsorption capacity if a adsorbate into adsorbent as specific time needed to maintain equilibrium interaction so the adsorption process undergo completion this show the effect of contact time on adsorption process . By using zeolite based geopolymers Cadmium removal was achieved at equilibrium contact time nearly 7 hours . Despite that fly ash-based geopolymers for lead removal gain equilibrium contact time at 120 min and remain constant after this period [69]. Another factor affecting adsorption process is the temperature: The nature of the processes either exothermic or endothermic depends on the adsorption equilibrium that is affected by the temperature used. It was shown that the uptake capacity of the adsorbate increases with the increasing in the temperatures. This occurs due to the enlargement of pores and activation of the sorbent surface. Removal of cadmium was increased with temperature range from 25°C to 45°C this was shown in a research by Javadian [70].

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

- **Langmuir Isotherm**

In 1916, 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.

**Assumptions of Langmuir Model:**

- 1- Monolayer adsorption: this means that each site of free surface of the used adsorbent can be occupied only by one adsorbate molecule when maximum adsorption was established.
- 2- Identical adsorbent surface: adsorbent has a uniform surface and all sites are energetically equivalent, so adsorption occurs through the same mechanism.
- 3- Adsorption is localized: when a molecule adsorbed at specific site on the adsorbate surface it will be independent on the occupation of other sites beside it, there is no movement of the adsorbate on the surface of adsorbent, but only molecule can be desorbed (moved again to solution) as it is a reversible process.

Usually Langmuir equation (1.1) is showed as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (1.1)$$

For the given abbreviations  $q_e$  is stated for heavy metal adsorbed per unit mass of activated carbon (mg/g) at equilibrium state, while  $q_m$  is the amount maximally measured for heavy metal adsorbed per one gram of activated carbon (mg/one gram), for  $C_e$  is the equilibrium concentration

of the heavy metal (mg/Liter), and finally  $b$  is always a constant in Langmuir equation (L/miligrams). This model based on showing that the adsorbent has homogeneously form of surface and identically sites for adsorption [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) :

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

For  $C_e$  it is an abbreviation stated on the equilibrium adsorbate concentration (mg/L), while for  $q_e$  it is quantity for heavy metal per one gram adsorbent (mg/one gram) when equilibrium was reached, finally constants for Freundlich equation are  $KF$  and  $n$ . as here  $n$  giving a constant number indicates how the favorable of the investigated adsorption pro adsorbent. While  $K_f$  is a constant with ((mg/g) multiplied by (L/mg) unit.

adsorption capacity for the adsorbent is related with  $(1/n)$  value while the slope  $(1/n)$  must have a range between [0 until reaching 1] to give an indication for surface heterogeneous property, because when it is value gets closer to zero more heterogeneous adsorption will occur [73].

### 3.1.7.2. Adsorption kinetic models

It is important thing to study Adsorption kinetics, as they show information about the system of adsorption behavior and also give how the rate at



which specific constituent will be removed by the investigated adsorbent. Also they provide indication about whether the adsorption process is chemical or physical and if specifically is the rate limiting step. Many models will describe the adsorption process. In this project we will use adsorption reaction models, which are mentioned below:

- **kinetic model called Pseudo--first order**

A kinetic modeling which called pseudo---first order is the earliest used model.

developed to the adsorption to show its kinetic process .

equation for this earliest model is :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1.3)$$

As we noticed  $q_e$  as well as  $q_t$  (mg/one gram ) are abbreviations stated for adsorption ability in equilibrium corresponding time  $t$  in minutes, respectively. While  $k_1$  is a constant of rate for the pseudo--first order with a unit of  $(\text{min}^{-1})$  [74].

- **kinetic model called Pseudo-second order**

It is usually performed to discuss how adsorption of metal ions with polar functional active groups for example, ketonic functional group, aldehydic ones , also dyes, herbicides, and phenols from the investigated aqueous solution if Langmuir equation was applied. A linear integral form is adopted :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1.4)$$

As mentioned above  $q_e$  in addition to  $q_t$  (mg per one gram) are related to adsorption ability at equilibrium in time  $t$  giving in minutes, respectively while  $K_2$  is constant for rate (gram per (miligram.minutes)) [75].

- **kinetic model called Second order**

usually the used form of second order rate equation can be applied to indicate adsorption process which based on uptake rate for the adsorbate.

This integrated form for the equation given by :

$$\frac{1}{C_t} = k_2 * t + \frac{1}{C_0} \quad (1.5)$$

Here  $C_0$  and  $C_t$  (mg per Liter) is the concentration of solute at time =zero and at time  $t$  is given by (min), respectively, while  $K_2$ \*(Liter per (mg.min)) is constant of adsorption rate [76].

### **3.1.7.3. Recent researches on heavy metal adsorption :**

For heavy metals removal from wastewater for treatment purposes , mainly polysaccharides especially chitosan, starch and its derivatives, also cyclodextrins, recently have attracted important attentions, due to their physico-chemical properties , as the presence of various reactive groups on the backbone chain Natural polymers present ,low cost and its availability however some disadvantages limit their use in practical applications of wastewater treatment, like their low surface area and it is difficult to separate them from the liquid phase. On the other hand magnetic sorbents, are easy to separate and manipulate in complex multiphase applications and have external magnetic field with a relatively high surface area. further

trials in developing adsorbents with superior properties would be included of magnetic particles into natural polymers, so combining the advantages of both materials. It was reported that nano-form for magnetic type material was functionalized with biopolymers such as chitossan [77-79].

Several methods are used for removing of heavy metals because of the new and effective separation technologies. ion exchange ,chemical precipitation , pre concentration , reverse osmosis , membrane filtration are the most used methods widely to remove heavy metals from wastewaters [80-82]

Also recently a promising cost-effective, sustainable, and eco safe technique for the removal of several types of organic and inorganic pollutants from wastewater is called biosorption method which has been regarded in treatment processes . also this process offers a number of advantages in comparing it to other conventional used methods [83].

Other recent researches focused on developing Numerous biomasses, like using algae, fungi , peat and other many agricultural wastes which have been tested as bio-sorbent to remove heavy metals in various experimental conditions , mainly because such biomasses have on their surface diverse functional groups, are available in large quantities and require only few steps of preparation In the case of biomass resulting from the production of biodiesel from biological sources , all these advantages are maintained. In addition, several previous studies [84-86].

## **3.2. Experimental set-up**

### **3.2.1. Materials**

#### **3.2.1.1. Precursor:**

The tubers tissues were utilized to be the precursor for developing of activated carbon by physically and chemically activating procedures. Our tuber powder was cleaned using water distilled in the lab for several times, drying as set on 150 °C in oven and then sieving the obtained dried powder through mesh with pores ranging from # eighteen to # thirty to remove the remained pulp and skin.

#### **3.2.1.2. Activators:**

- Potassium hydroxide KOH
- Zinc chloride ZnCl<sub>2</sub>

All chemical reagents for activation of powdered tubers were of 98% purity.

#### **3.2.1.3. The used Tube--Furnace :**

Tubular--regulated-furnace (Lindberg` 9001) with a 0.25 cm thick cylindrical stainless steel tube ( four cm inner diameter and seventy four cm length).

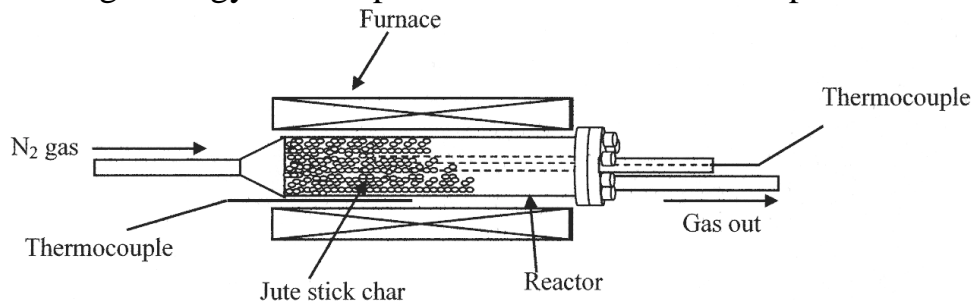
#### **3.2.1.4. Adsorbate and Chemicals**

Heavy metals (Cd,Cu ,Cr and Pb)was purchased from Al - Najah

University Chemicals Warehouse for our experimental steps used hydrochloric acid,  $I_2$  as well as sodium--hydroxide, sodium thiosulfate, which were of analytical degree for this activation process

### 3.2.1.5. Physical activation

For physical activation the production of charcoal in carbonization step was performed using carbon gaseous activating agent nitrogen gas. Between carbon atom and the gas an Oxidative reaction was completed; which increasing the pore numbers in the carbonized material. This procedure is safe eco system since no pollution occurred chemical materials were included ; but it has several limitations as the low carbon yield and high energy consumption will be needed in this process.



**Figure (3. 1) :** Tube furnace scheme

As long time and temperature with high degree are needed in carbonization-activation to utilize activated carbon comparing to chemical activation . 80 g of dried powdered tubers was placed in crucible which must be flat and in the center of calibrated furnace this sample was inserted. This programming steps were set as mentioned in Table (3.1).

**Table (3. 1): carbonization/activation program set-up**

Value	Parameter
450 °C	Activation temperature
20 °C/min	Heating rate
70 min	Holding time
0.2L/min	N <sub>2</sub> flow rate

### 3.2.1.6. Chemical activation

For application of activation Chemically this will produce activated charcoal with larger number of pores by impregnation of the precursor with the following chemical agents ; potassium--hydroxide , and zinc--chloride . because of having dehydrating characteristics promoting pyrolytical decomposing process and stopping tar-formation and also volatile--organic compounds to be formed in activation as high temperature was set up .the resulted activated carbon yield will be higher .

- **Carbon Activation by Zinc Chloride**

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

In this work, impregnation with zinc chloride was performed using temperature 70°C and placing it water bath until excess water was evaporated. After that this sample was filtered and dried above one hundred Celsius centigrade an available in our laboratory-oven . then carbonized at temperature 450°C for 50 min. The carbonized product was washed with 0.50 M hydrochloric acid solution, distilled

water after that was used to wash it and finally cooled so removing residual inorganic from activating agent was completed. Drying and stored the final product for further use was achieved.

- **Chemical activation by KOH of *Asphodelus ramosus* tubers**

A sample of 15g dried *Asphodelus ramosus* 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. Two hours refluxing for the solution at 60 °C, then it was left to cool down before decanting it .In an oven one hour drying for the wet solid at 110 °C. This sample is carbonized and activated under 450 °C temperature for 50 min.

### **3.2.2. Adsorption kinetic of heavy metals onto activated carbon prepared from *Asphodelus ramosus* tubers**

#### **3.2.2.1. Determination method of heavy metals Concentration**

For each Heavy metals the concentration was measured using Flame Atomic Absorption (ThermoScientific iCE3000, Type iCE3500AA System).

#### **3.2.2.2. Heavy metals Standard solutions preparation**

Preparation for each heavy metal stock aqueous solution of (1000 ppm) was performed then serial standard solutions with concentrations in the range (zero-80) ppm were obtained.

For each heavy metal The initial as well as the final concentrations were measured. The quantity adsorbed in equilibrium-stage,  $q_e$  (mg/one gram), was mathematically estimated by [87]:

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

Here  $q_e$  : abbreviation stated on solid phase equilibrium concentration (miligrams of heavy metal per one gram of activated carbon)

The Intial heavy metal concentration in (ppm) is abbreviated by  $C_o$  while  $C_{eq}$  is concentration of heavy metal (ppm) occurred at Equilibrium volume heavy metal solution volume is abbreviated by  $V$  and  $W$  is stand as abbreviation for activated carbon mass in grams.

The % removal was estimated basing on equation below:

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

$C_o$  concentration initially recorded for heavy metal

$C_e$  is an equilibrium heavy metal

### **3.2.3. Experimental set up for adsorption**

#### **3.2.3.1. Assessment for pH effect**

Initial pH used in adsorption will affect the adsorption capacity this was estimated throughout pH ranging values 2--12. The value of pH controlled by adding sodium hydroxide or sulphuric acid solution, heavy metals



solutions (50 mL, 50 ppm each) were added to adsorbent samples (0.2 g). The shaking of mixtures was carried out for 3 hr at 25°C.

### **3.2.3.2. Effect of Temperature**

If temperature changes during adsorption process this will affect the capacity of heavy metal adsorption this parameter was studied using (50 milliliter with concentration of 50 ppm for each heavy metal) which introduced into a sample of adsorbent (0.2--gram) on pH<sub>value</sub> equal to 4. Shaking then for 3 h at several temperatures ranges between 0 and 45°C.

### **3.2.3.3. adsorption Kinetics by study the effect of contact time**

Usually time affects the adsorption. This parameter was studied using solution of 50 milliliter with concentration of 50 ppm for each heavy metal. This was added to adsorbent sample (0.2 g) at adjusted pH equal to 4. The shaking then took place at 25°C.

A sample of 1 mL from each the clear solutions were pipetted out at several time intervals until equilibrium was established.

### **3.2.3.4. Effect of heavy metal concentration**

In each adsorption experiment, different concentration ranging at (5- 80 ppm) of heavy metals then 0.2g adsorbent was placed, with the used pH equal to 4. shaking the flasks then carried out at 25°C until equilibrium was established.

For concentrations of heavy metals each initial and final were measured.

### 3.3. Resulted data & discussion

#### 3.3.1. surface area estimated by Iodine #:

Given data in table --3.2 showed the best surface area of the prepared activated--carbon specimens was when zinc--chloride has been utilized as activating process which result was 506.5 m<sup>2</sup>/g followed by activation using KOH that gave 480.25 mg/g surface area. For comparison commercial ctivated carbon CAC had 392.75 mg /g using this iodine number test.

**Table (3. 2): surface area of several AC corresponding to iodine # testing.**

Specimen	Surface--area
	( m <sup>2</sup>   gram)
Zn Cl 2	506.5
K OH	480.25
Physically activated	422.56
Commercial activated carbon	392.75

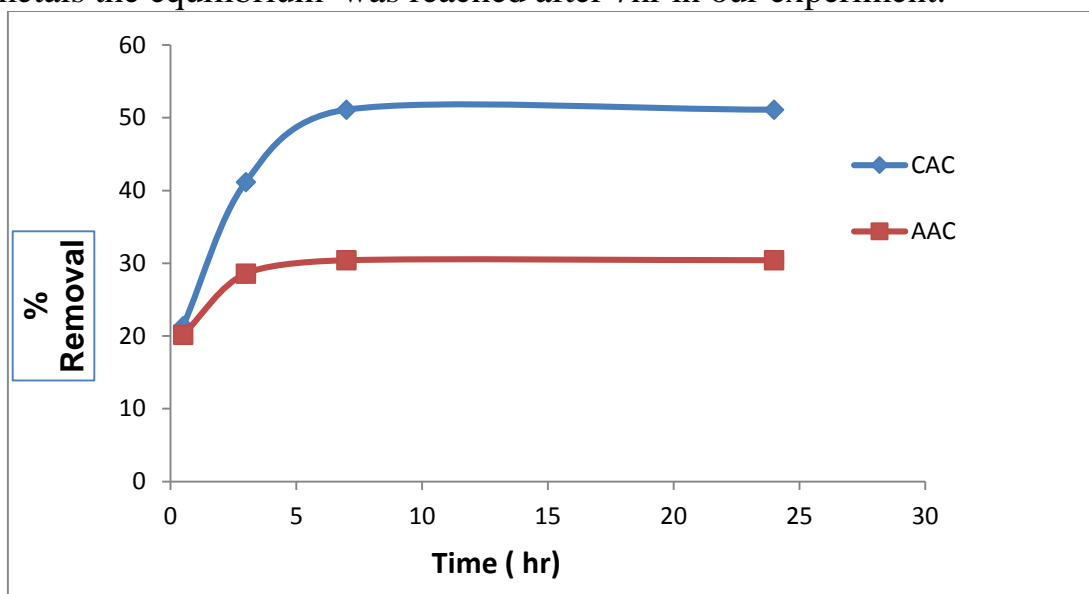
#### 3.3.2. Heavy` metals adsorption ability onto AC prepared from

*Asphodelus ramosus* tubers

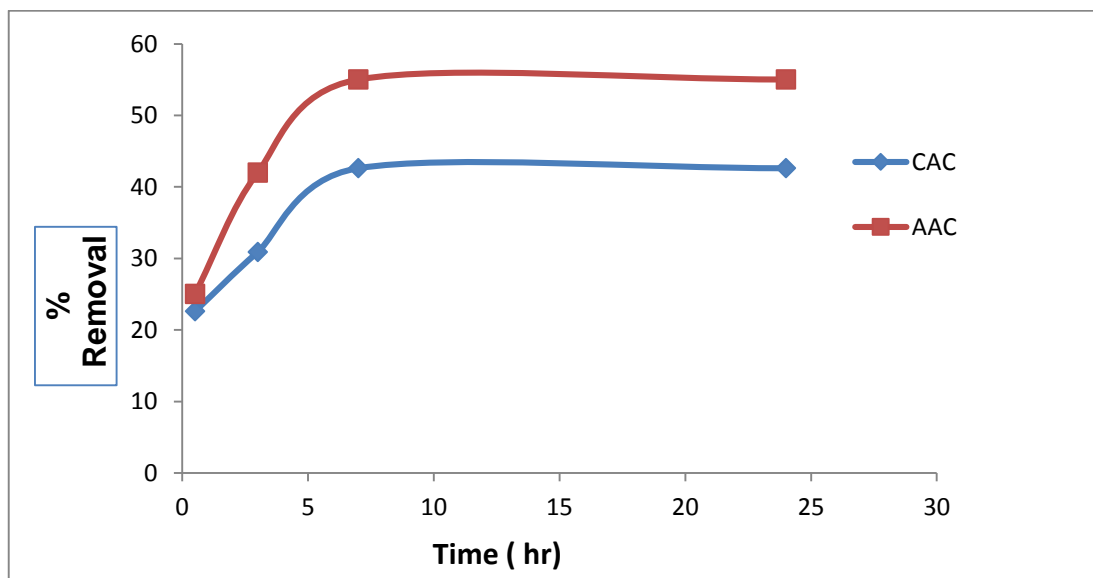
##### 3.3.2.1. Contact Time effect on adsorption capacity

As usually shown in researches contact time will affect removing percentage % of each tested metals from the prepared solution .This result was shown in Fig (3.2-3.5).

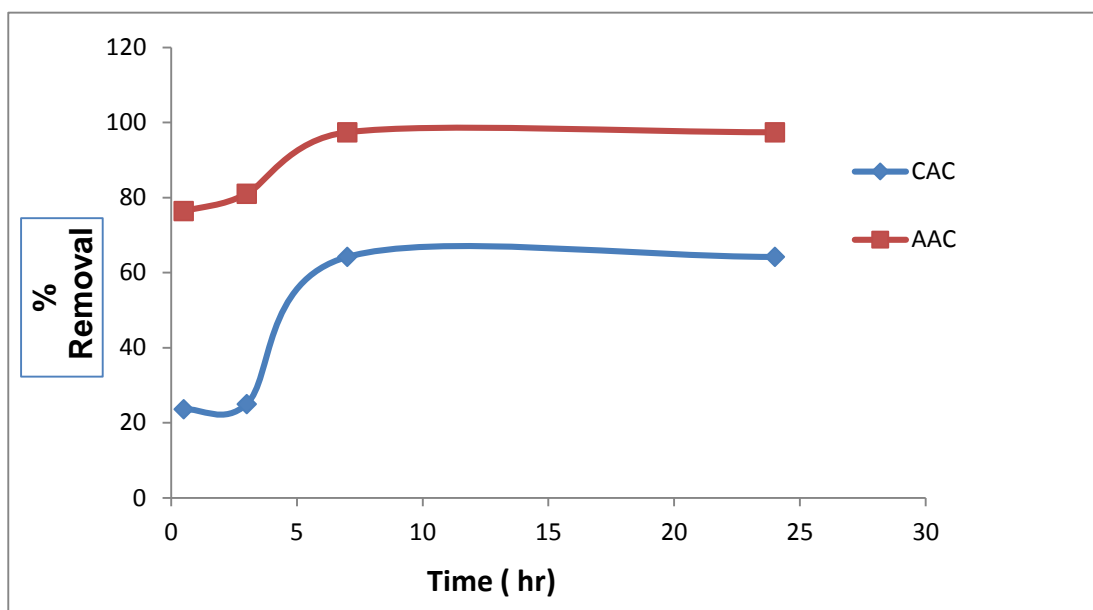
The adsorbed amount of all tested metal's ions ; Cr, Cu, pb and Cd onto AAC and CAC increases as contact time increased, as shown in Fig(3.2-3.5) until reaching equilibrium after 7hr, it was observed that for all tested metals the equilibrium was reached after 7hr in our experiment.



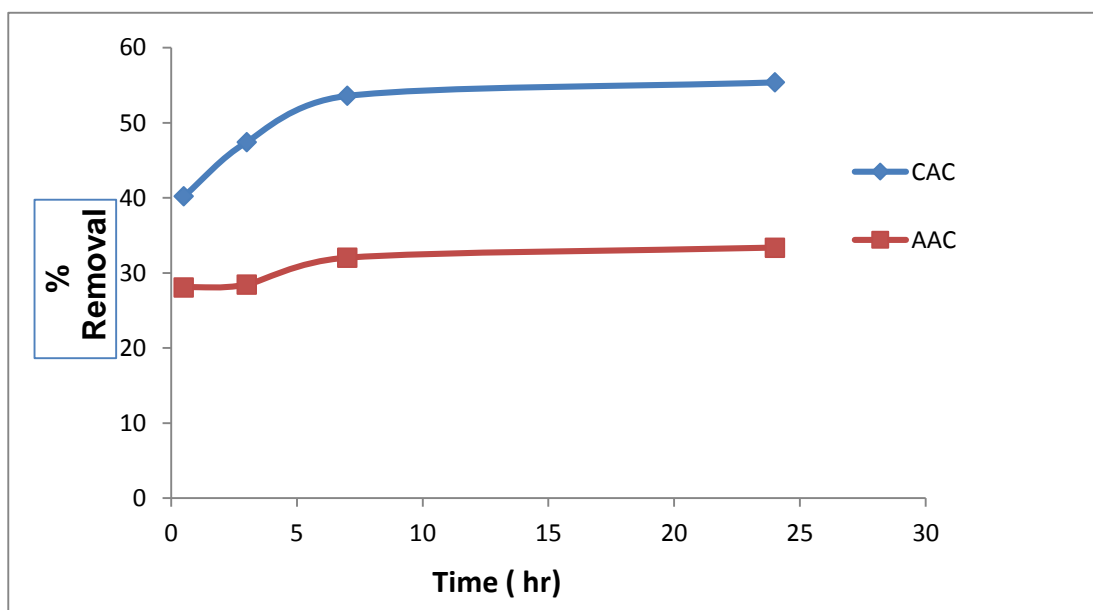
**Figure (3. 2) :** contact time action on Cr ( III ) removal by AAC and CAC on (conc.. 50 ppm, initial pH;; 4, temperature;; 25 °C ).



**Figure (3. 3) :** contact time action on Cu ( II ) removal by AAC and CAC on (conc.. 50 ppm, initial pH;; 4, temperature;; 25 °C ).



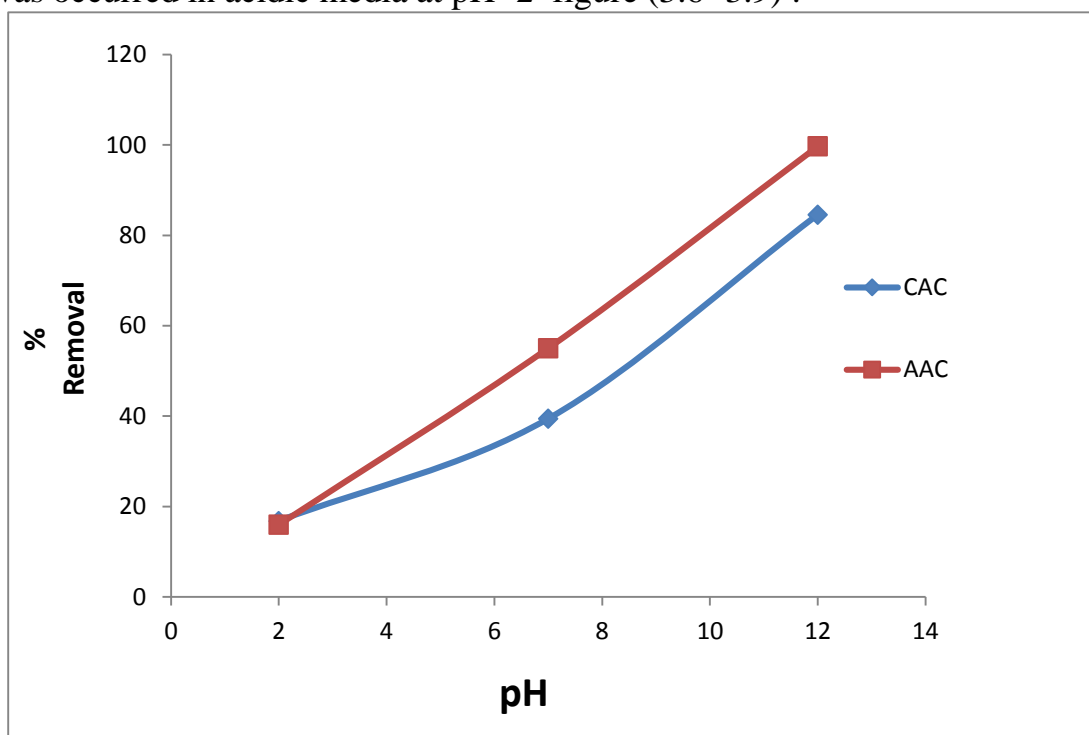
**Figure (3.4) :** contact time action on pb( II ) removal by AAC and CAC on (conc.. 50 ppm, initial pH;; 4, temperature;; 25 °C ).



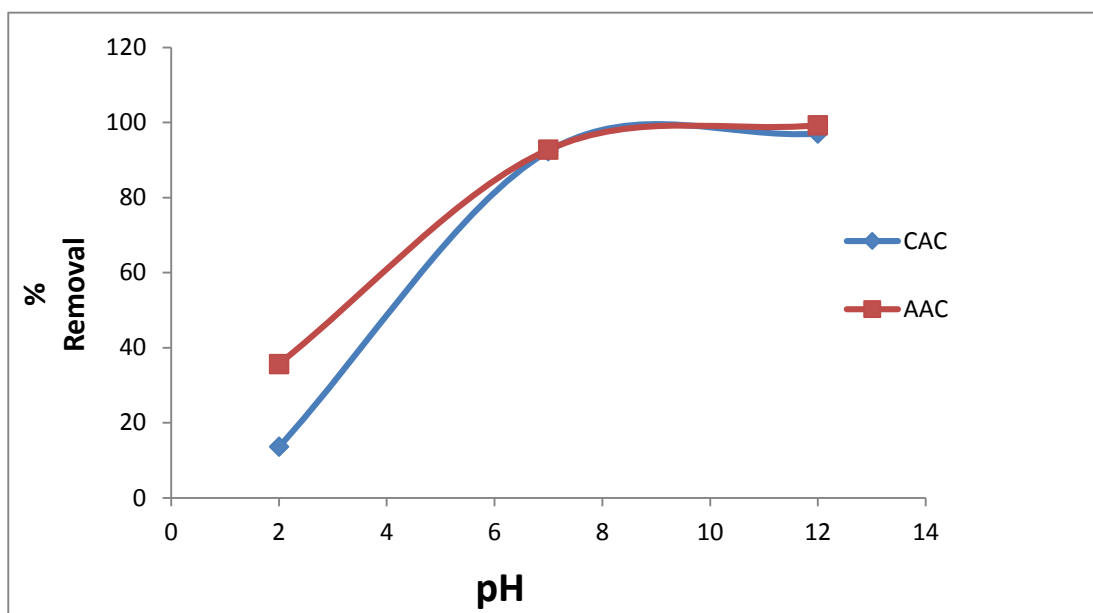
**Figure (3.5) :** contact time action on Cd ( II ) removal by AAC and CAC on (conc.. 50 ppm, initial pH;; 4, temperature;; 25 °C ).

### 3.3.2.2. pH Action on adsorption results

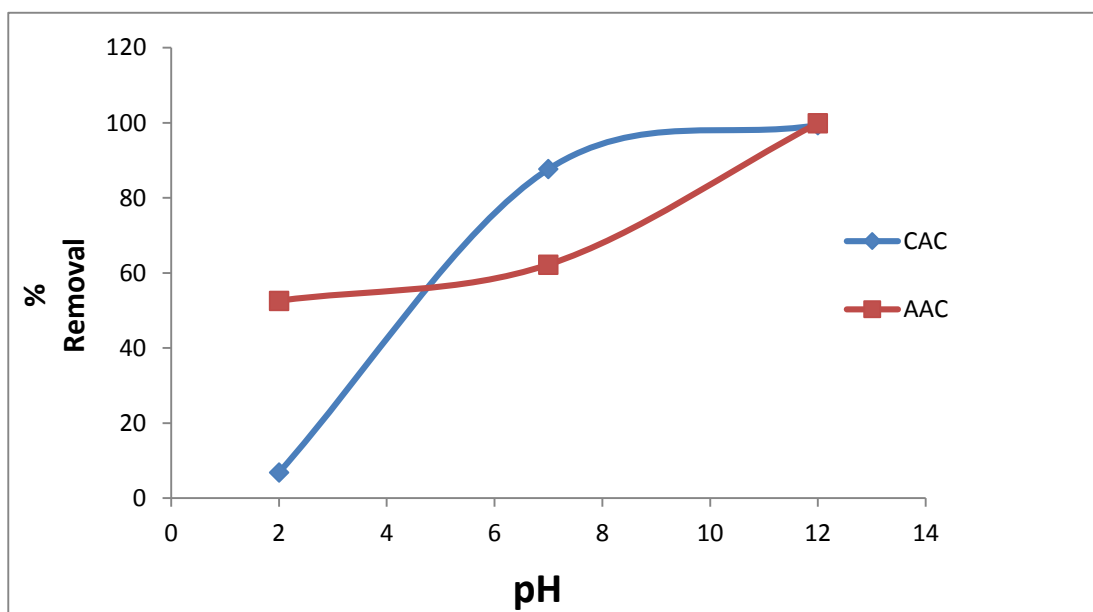
For each tested heavy metal's the action of pH onto AAC and CAC was evaluated in (2-12 ) range adjusting of pH was performed using sulfuric-- acid and sodium--hydroxide . The study of pH action in removal was carried out using 0.2g AAC and CAC at an adsorption time 7hr to reach equilibrium, it was obvious that all four heavy metals showed higher adsorption onto both AAC and CAC in alkaline media at pH=12 while the least adsorption capacity was occurred in acidic media at pH=2 figure (3.6- 3.9) :



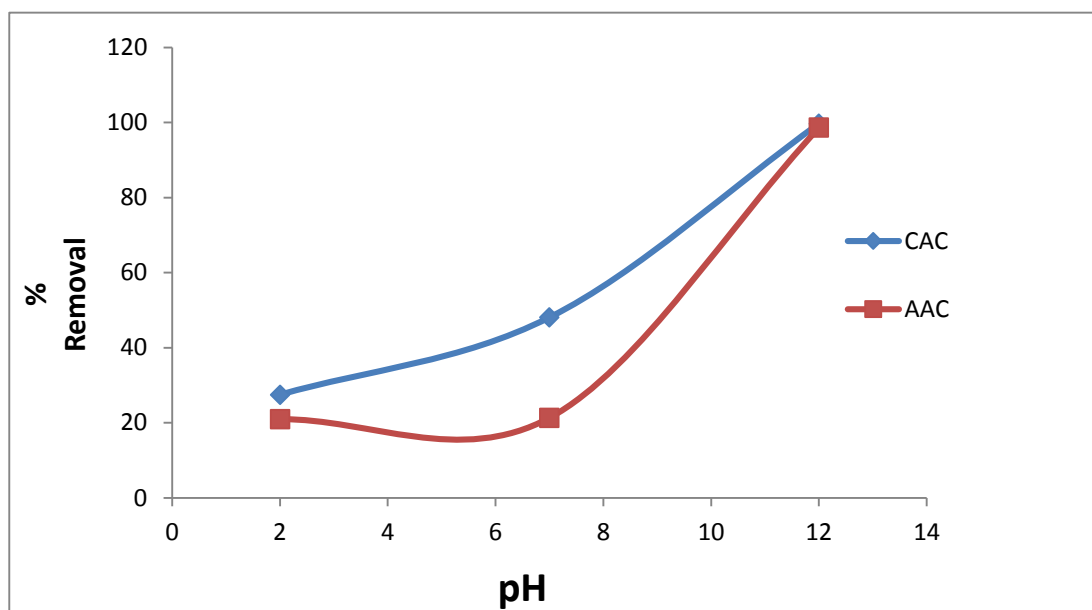
**Figure (3. 6):** pH action on Cr(III) removal by AAC and CAC on ( conc;.50 ppm, temperature;. 25 °C, contact--time: 7hr )



**Figure (3. 7):** pH action on pb (II) removal by AAC and CAC on (conc;.50 ppm, temperature;. 25 °C, contact—time;. 7hr )



**Figure (3. 8):** pH action on Cu(II) removal by AAC and CAC on ( conc;.50 ppm, temperature;.25 °C, contact time;. 7hr )



**Figure (3. 9):** pH action on Cd(II) removal by AAC and CAC on (conc;.50 ppm, temperature;. 25 °C, contact time;. 7hr )

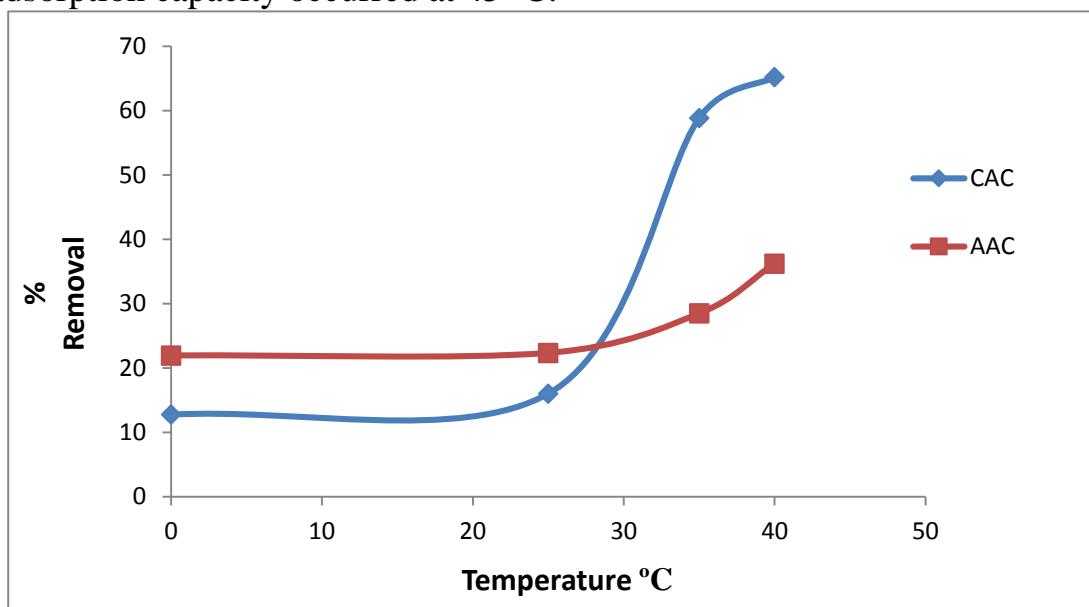
For all examined heavy metals when pH value was acidic the concentration of protons was high and for each studied metal the binding sites became positively charged and repelled the Cd (II), pb (II), cu (III) and Cr (II) cations. While increasing in pH value , the negative charge density on the adsorbent will increase because of the deprotonation of the binding sites available for each heavy metal, an as a result this increased metal adsorption. The maximum adsorption observed in pH value equal to 12 and the resulted reduction in adsorption capacity was obviously because of the the partial hydrolysis of metal ions.

So at low value of pH or in other expression acidic pH, both adsorbent and metal ions presented as species with positively-charged sites .As a result for this , the electrostatic repulsion might occur and this cause reduction in the adsorption capacity. Also the proton may obviously compete with metal ions to bind with these active sites.

### 3.3.2.3. Effect of Temperature

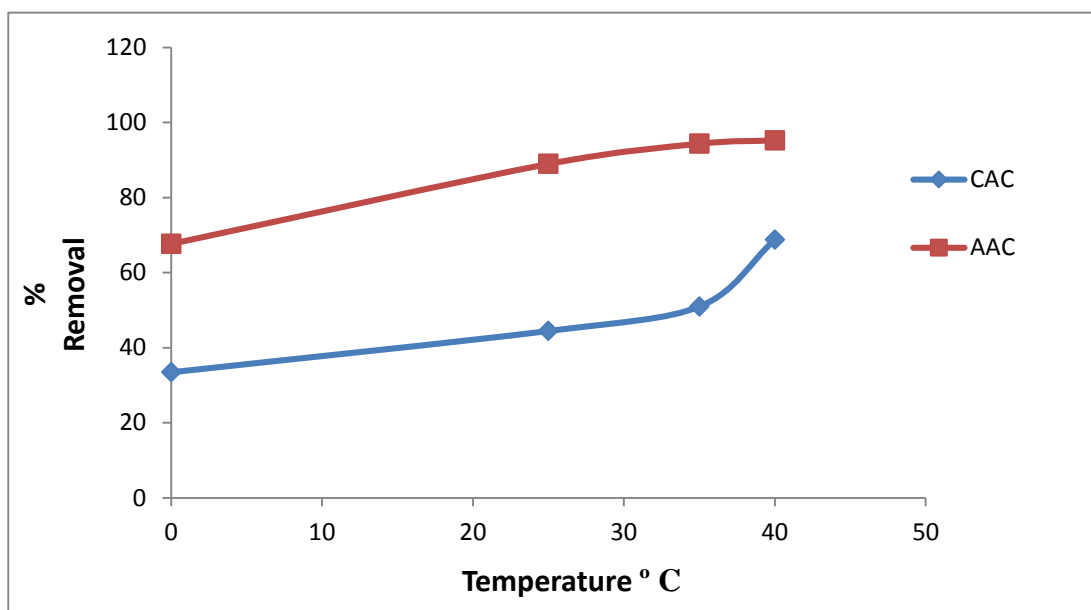
Temperature effect on adsorption of the four heavy metals onto AAC and CAC were estimated in 0--45 °C range. Figure (3.10 - 3.13) viewed these resulted data.

Its seems that for all heavy metals the adsorption onto both AAC and CAC was increased with the increasing in temperature as maximum adsorption capacity occurred at 45 °C.

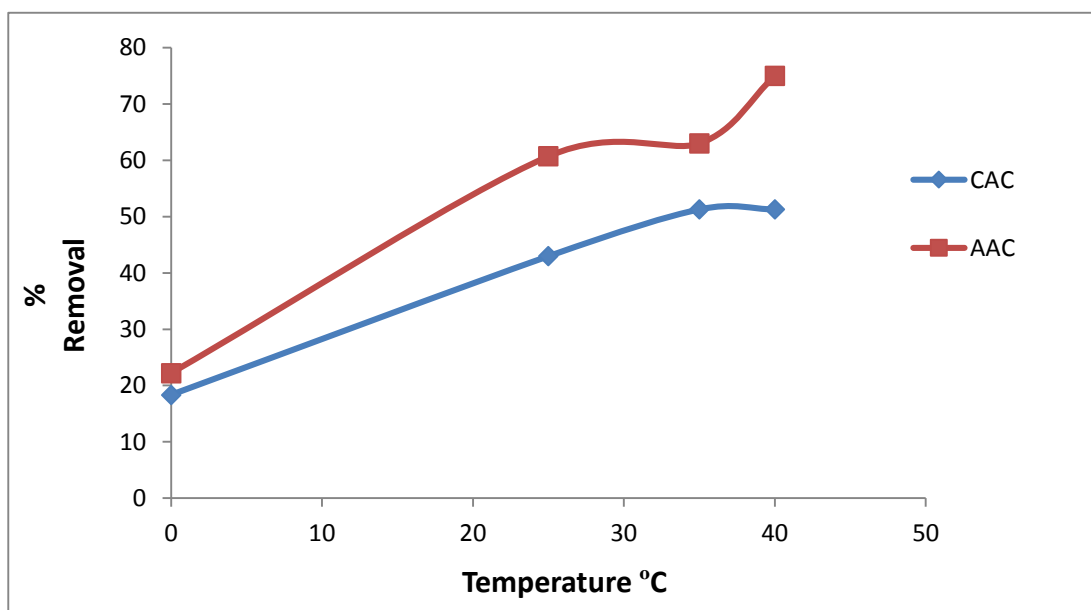


**Figure` (3. 10):** temperature action on Cr(III) removal by AAC and CAC on (conc;. 50 ppm, initial pH;. 4, time for contact;. 7hr.

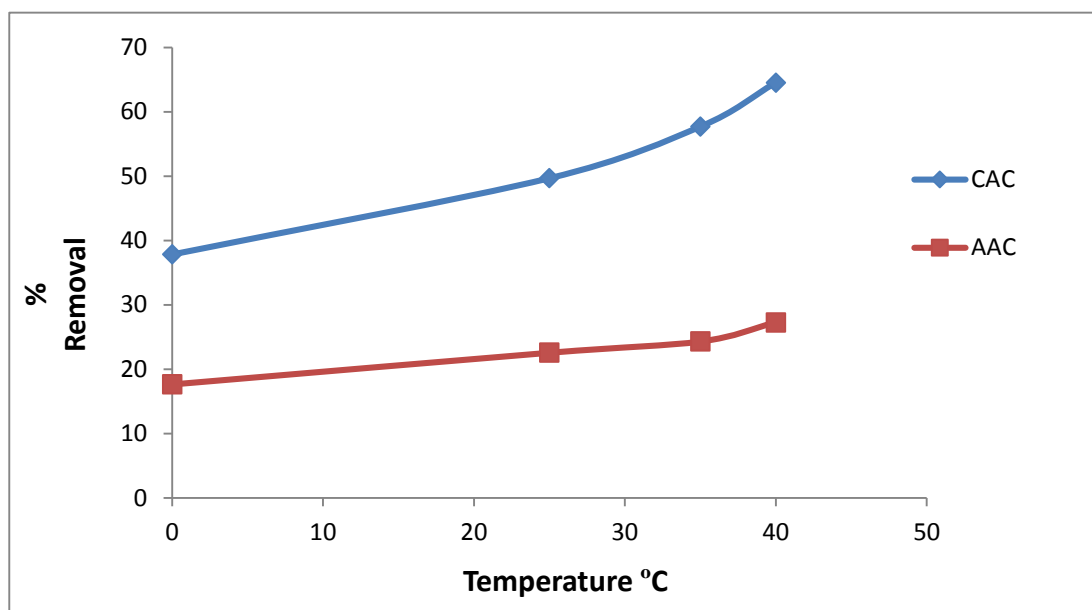




**Figure` (3. 11):** temperature action on pb(II) removal by AAC and CAC on (conc;. 50 ppm, initial pH;. 4, time for contact;.7hr.



**Figure` (3. 12):** temperature action on Cu(II) removal by AAC and CAC on (conc;. 50 ppm, initial pH;. 4, time for contact;.7hr.



**Figure` (3. 13):** temperature action on Cu(II) removal by AAC and CAC on (conc;. 50 ppm, initial pH;. 4, time for contact;.7hr.

Thus, at high temperature ,the movement of all tested heavy metal ions into the activated carbon particles increases with the increasing in temperature because the increasing temperature caused complexation between heavy metallic ion` and the active sites of activated carbon to occur easier . Also this can be explained as expansion within the active surface site when the temperature increases [88].

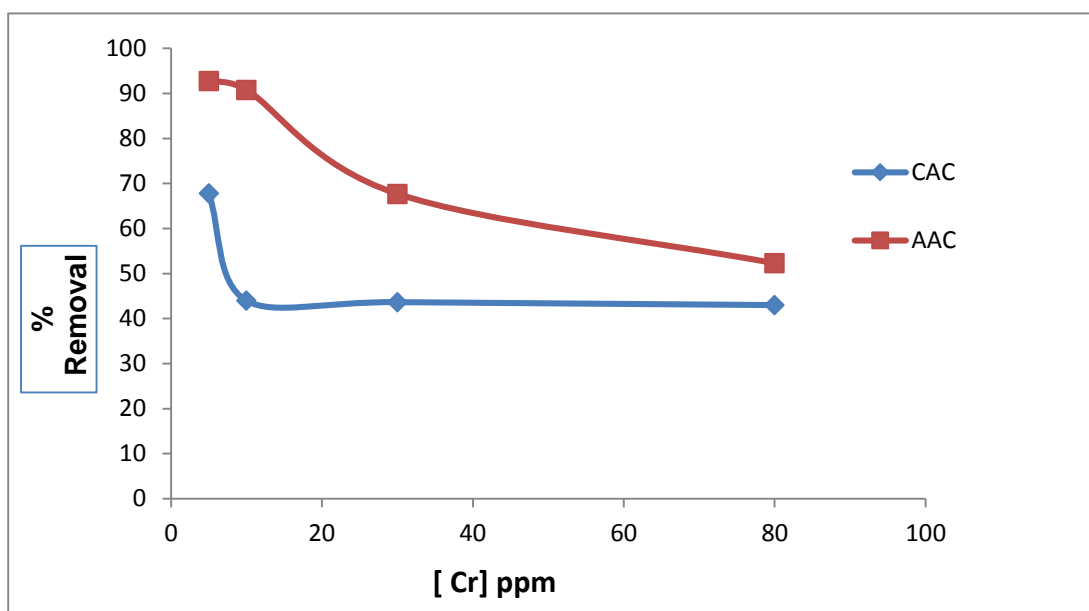
#### **3.3.2.4. concentrations effect on heavy adsorption capacity**

figures (3.14-3.17) show the action of concentration of each heavy metal on % removing in equilibrium state. It was obvious as the concentration was elevated a decrease in %removal .

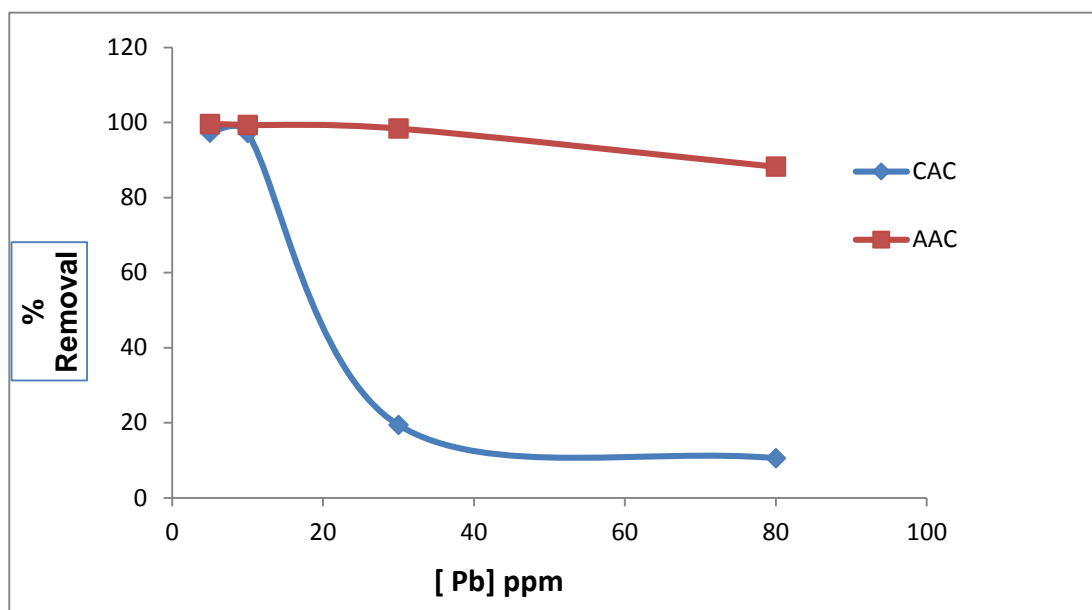
Increases the concentration in [5 mg/L --80 mg/L] range , showed percentage decreasing of removal in [97.3 %--10.6%] in CAC and [99.65% --88.26%] for AAC in case of pb(II) . while this decreasing was from

67.8% to 43% for CAC and from 92.85% to 52.3% for AAC in case of Cr(III).

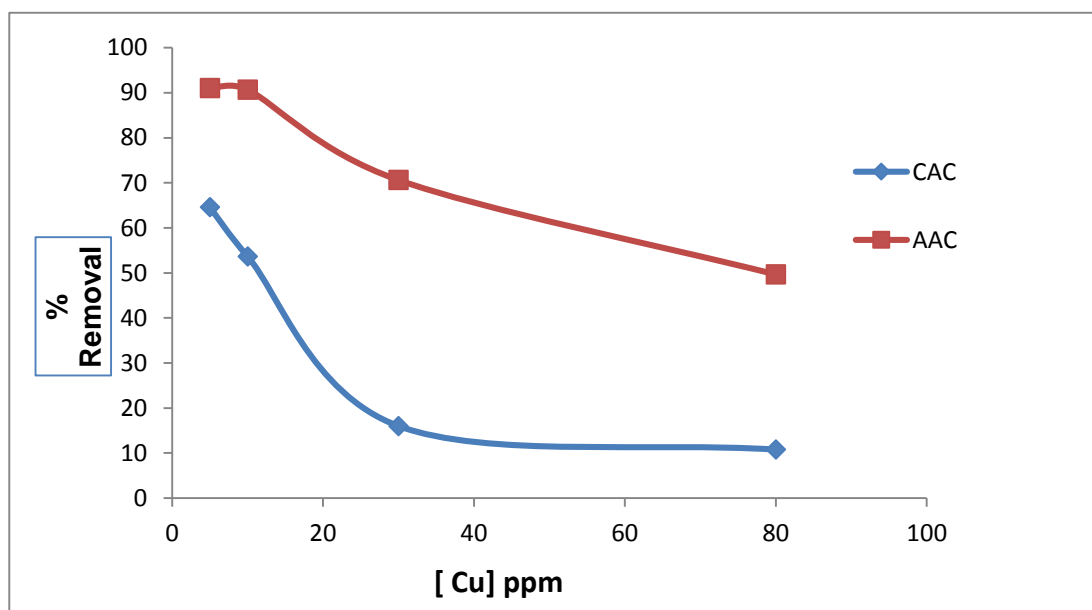
On the other hand the decrease of % Removal was 64.6% to 10.8% for CAC and was 91.06% to 49.66% for AAC in case of Cu(II). Finally this decreasing in % Removal was 75.47% to 30.6% for CAC and 57.06% to 31.58% for AAC in case of Cd(II).



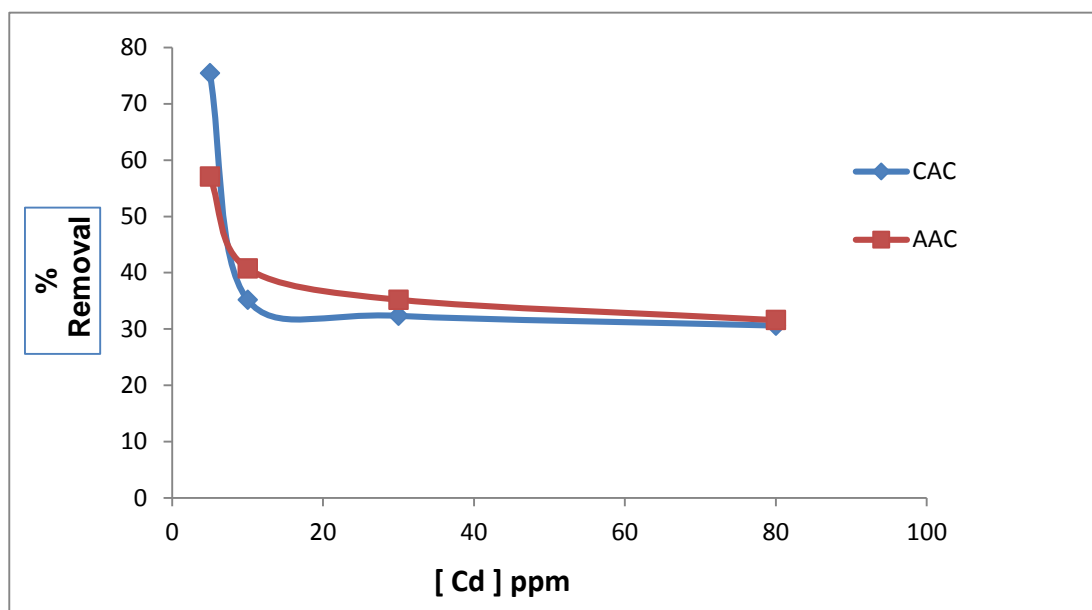
**Figure (3. 14) :** Effect of Cr(III) concentration on % removal by AAC and CAC at (initial adsorbent dose: 0.2 g, initial pH: 4, contact time: 7hr, Temperature 25 °C).



**Figure (3. 15) :** Effect of pb(II) concentration on % removal by AAC and CAC at (initial adsorbent dose: 0.2 g, initial pH: 4, contact time: 7hr, Temperature 25 °C).



**Figure (3. 16) :** Effect of Cu(II) concentration on % removal by AAC and CAA at (initial adsorbent dose: 0.2 g, initial pH: 4, contact time: 7hr, Temperature 25 °C).



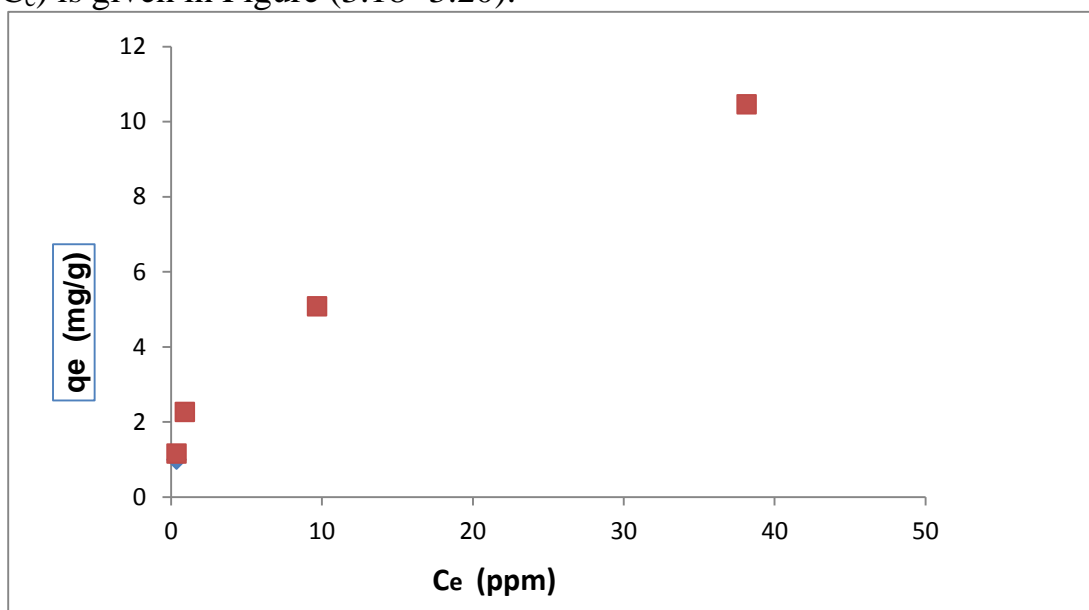
**Figure (3. 17):** Effect of Cd(II) concentration on % removal by AAC and CAA at (initial adsorbent dose: 0.2 g, initial pH: 4, contact time: 7hr, Temperature 25 °C).

For all investigated heavy metals it was observed that as the used metal ion concentrations was lower, better removal efficiency was achieved as higher number of sites are available for metal ions to be adsorbed. On the other side as concentrations become higher for metal ions the number the available sites for adsorption became less . The max-removal% of copper (II) and cadmium (II) are 87% and 82% respectively at 5ppm . as a result % removed metal ions was dependent on metal ions concentration that used at the beginning and will be decreased with this concentration increasing.

The reasonable comment for the previous results was that saturation of metal ion binding adsorption sites occurred rapidly at specific concentration of metal ions and an equilibrium state between adsorbate and adsorbent was achieved after that [89].

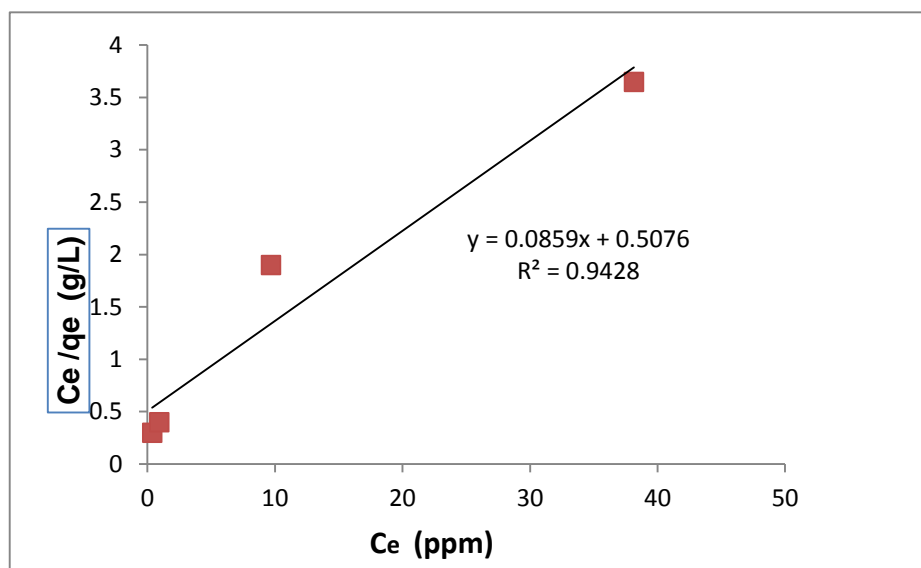
### 3.3.3. Adsorption isotherms

In our project both Langmuir` and Freundlich` isotherm-models were used for the characterization of adsorption process and to investigate how the amounts of Cr(III) adsorbed ( $q_e$ ) and its equilibrium concentration were related to each other at specific temperature which was 25 °C onto AAC ( $C_e$ ) is given in Figure (3.18- 3.20):



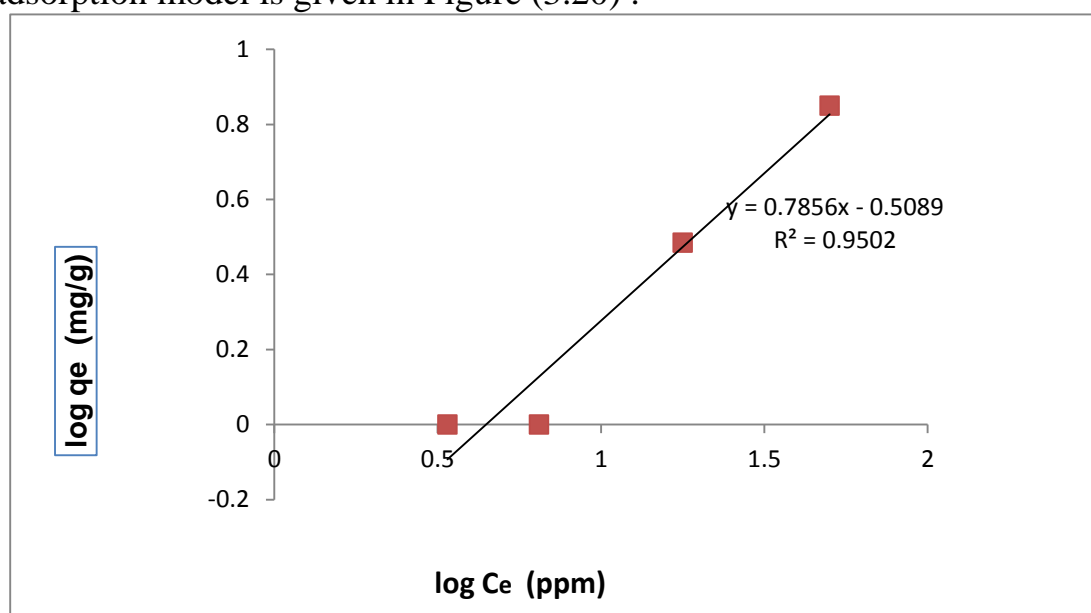
**Figure (3. 18):** adsorption-isotherm at equilibrium state of Cr(III) onto AAC at (temperature;; 25 oC, initial pH 4 , after 7hr and solid:: liquid ratio 0.2 g::50 mL)

Adsorption isotherm for chromium onto AAC at 25 °C using Languimer adsorption model is given in Figure (3.19):



**Figure (3. 19):** Plotting of Langmuir' for Cr(III) adsorption onto AAC (temperature;; 25 °C, initial pH;; 4 and solid:: liquid ratio 0.2g ::50 mL)

Adsorption isotherm for chromium onto AAC at 25 °C using Freundlich adsorption model is given in Figure (3.20) :



**Figure (3. 20):** Plotting of Freundlich' plot for Cr(III) adsorption onto AAC (temperature;; 25 °C, initial pH;; 4 and solid:: liquid ratio: 0.2 g:: 50 mL).

The investigated parameters for adsorption isotherm study were calculated from the obtained slope and the intercept for the linear plots

using both the Langmuir and Freundlich equations, together with the  $R^2$  values are given in Table (3.3) :

**Table (3. 3): Isotherms constants for Cr(III) adsorption onto AAC**

Langmuir` Isotherm			Freundlich` Isotherm		
$R^2$	$K_L$ (L/mg)	$Q_{max}$ (mg/g)	$R^2$	$K_F$ $((\text{mg/g})(\text{L/mg})^{1/n})$	N
0.942	0.507	11.76	0.995	0.31	1.273

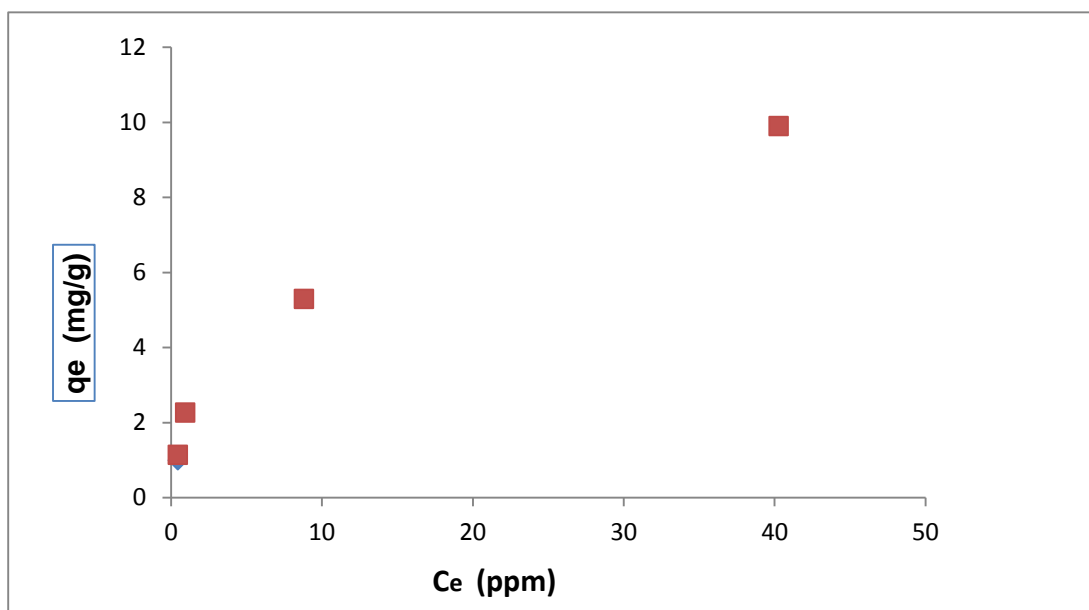
$R^2$  estimated numbers from Freundlich isotherm is suitable result with the data better than Langmuir`. The Freundlich` modeling shows that adsorption may occur due to electrostatic complexation between the investigated heavy metal ion and the bulk functional groups of activated carbon which is negatively charged and so adsorption occurred in multilayer system rather one layer.

The adsorption was tended to fit Freundlich better as constant (n) placed in arrange of (1--10). Bigger value of n (smaller value of  $1/n$ ) indicated stronger interaction between the adsorbent and the adsorbate. From Table 3.3 (n) value was seen to place between (1 -10) range showing valuable adsorption of cadmium ion on the prepared activated carbon.

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

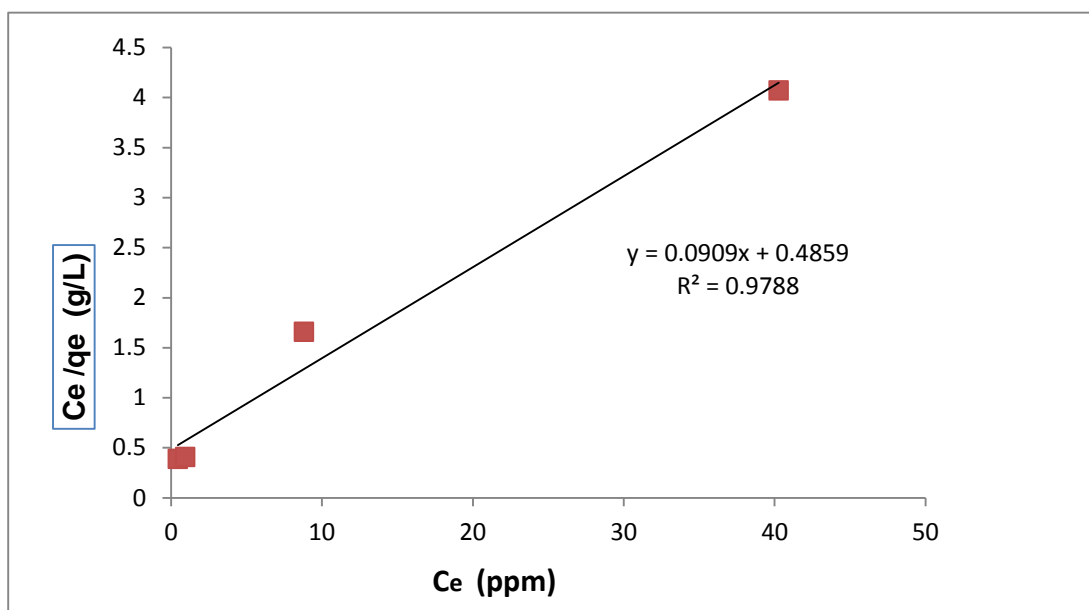


Langmuir and Freundlich isotherm models were used to describe the adsorption isotherm to study relationship between the amounts of copper adsorbed ( $q_e$ ) and its equilibrium concentration in solution at 25 °C onto AAC ( $C_e$ ) is given in Figure (3.21-3.23):



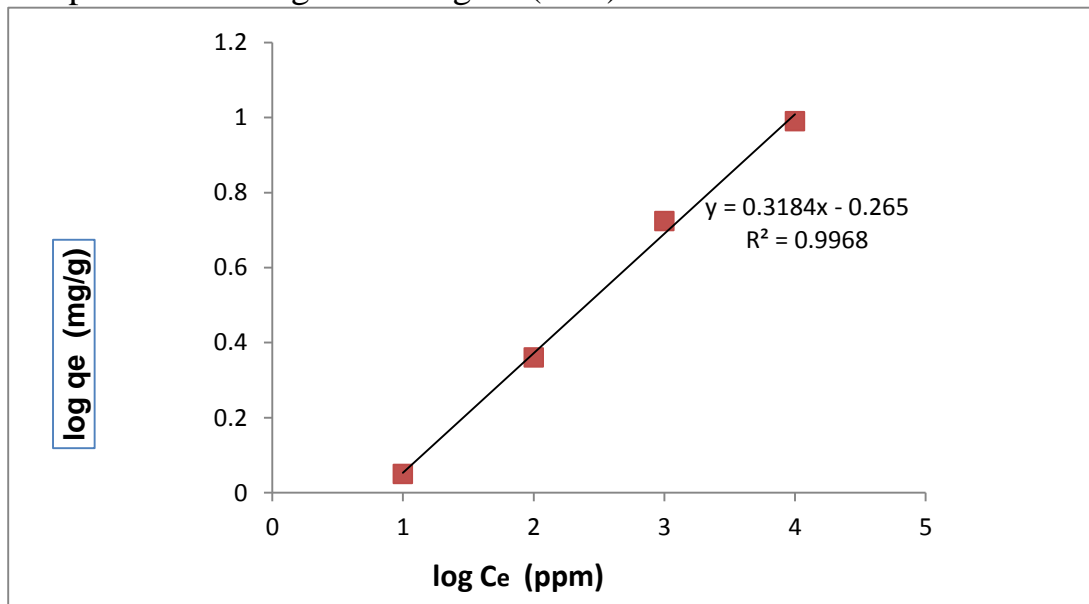
**Figure (3. 21):** adsorption-isotherm at equilibrium state of Cu(II) onto AAC at (temperature;; 25 oC, initial pH 4 , after 7hr and solid:: liquid ratio 0.2 g::50 mL)

Adsorption isotherm for chromium onto AAC at 25 °C using Languimer adsorption model is given in Figure (3.22) :



**Figure (3. 22):** Plotting of Langmuir' for Cu(II) adsorption onto AAC (temperature;; 25 ° C, initial pH;; 4 and solid:: liquid ratio 0.2g ::50 mL)

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



**Figure (3. 23):** Plotting of Freundlich' plot for Cu(II) adsorption onto AAC (temperature;; 25 ° C, initial pH;; 4 and solid:: liquid ratio: 0.2 g:: 50 mL).

As mentioned above isotherm parameters for adsorption were calculated from the slope and the obtained intercept of the linear plots using the linear both Langmuir and Freundlich equations, together with the  $R^2$  values are given in Table (3.4) :

**Table (3. 4): Isotherms constants for Cu(II) adsorption onto AAC**

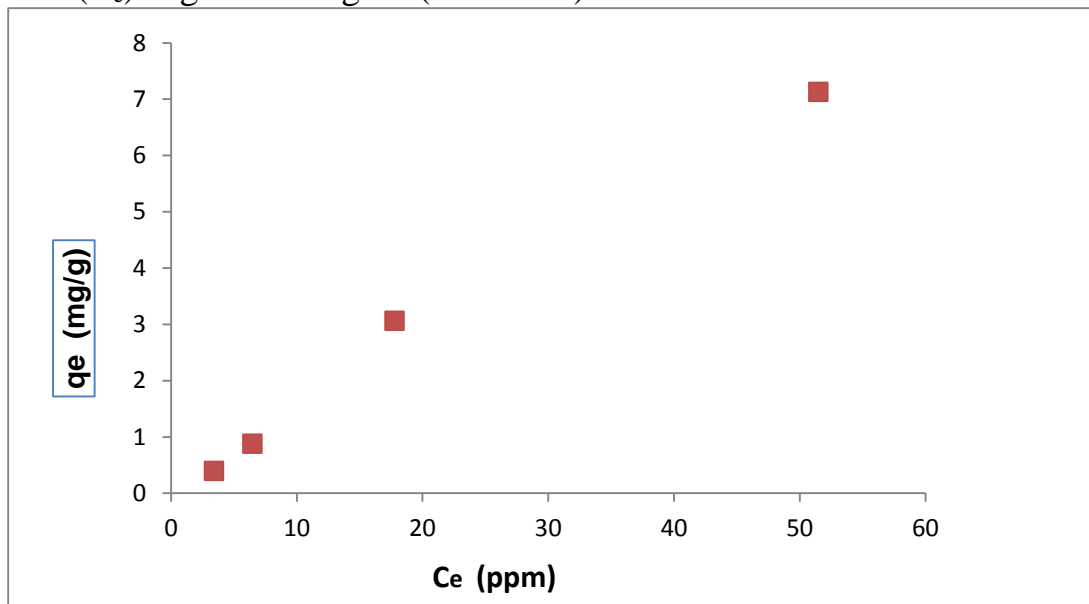
Langmuir` Isotherm			Freundlich` Isotherm		
$R^2$	$K_L$ (L/mg)	$Q_{max}$ (mg/g)	$R^2$	$K_F$ $((mg/g)(L/mg)^{1/n})$	N
0.978	0.485	11.11	0.996	0.543	3.144

$R^2$  estimated numbers from Freundlich isotherm is suitable result with the data better than Langmuir`. The Freundlich` modeling shows that adsorption may occur due to electrostatic complexation between the investigated heavy metal ion and the bulk functional groups of activated carbon which is negatively charged and so adsorption occurred in multilayer system rather one layer.

The adsorption was tended to fit Freundlich better as constant (n) placed in arrange of (1--10). Bigger value of n (smaller value of  $1/n$ ) indicated stronger interaction between the adsorbent and the adsorbate. From Table 3.4 (n) value was seen to place between (1 -10) range showing valuable adsorption of cadmium ion on the prepared activated carbon.

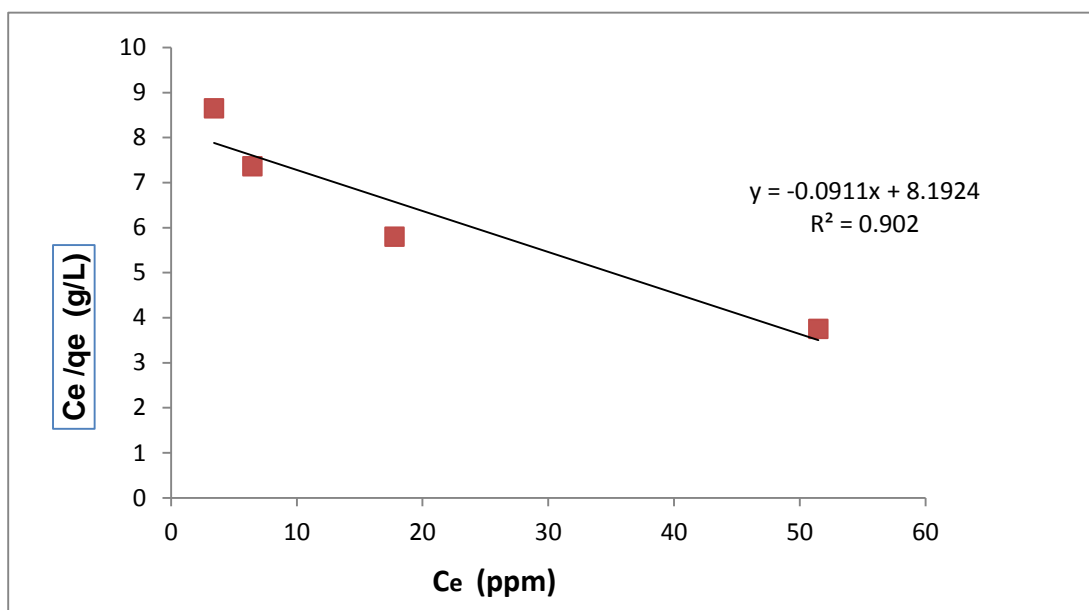
Langmuir` and Freundlich` modeling forms were used to characterize the adsorption process in order to know how amounts of cadmium adsorbed

( $q_e$ ) was related with the reached concentration in equilibrium state onto AAC ( $C_e$ ) is given in Figure (3.24-3.26):



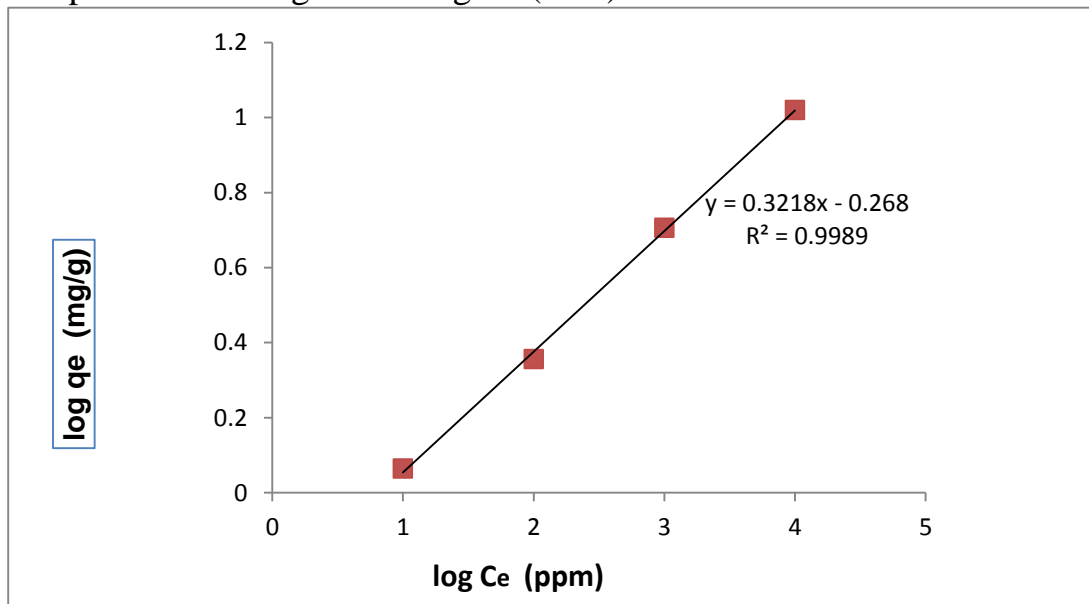
**Figure (3. 24):** adsorption-isotherm at equilibrium state of Cd(II) onto AAC at (temperature;; 25 oC, initial pH 4 , after 7hr and solid:: liquid ratio 0.2 g::50 mL)

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



**Figure (3. 25):** Plotting of Langmuir' for Cd(II) adsorption onto AAC (temperature;; 25 ° C, initial pH;; 4 and solid:: liquid ratio 0.2g ::50 mL)

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



**Figure (3. 26):** Plotting of Freundlich' plot for Cd(II) adsorption onto AAC (temperature;; 25 ° C, initial pH;; 4 and solid:: liquid ratio: 0.2 g:: 50 mL).

The studied parameter's for adsorption isotherm were obtained from slope and intercept of the obtained linear plotting curve using the linear zed

form of Langmuir` and Freundlich` equation`s, together with the  $R^2$  numbers are given in Table (3.5)

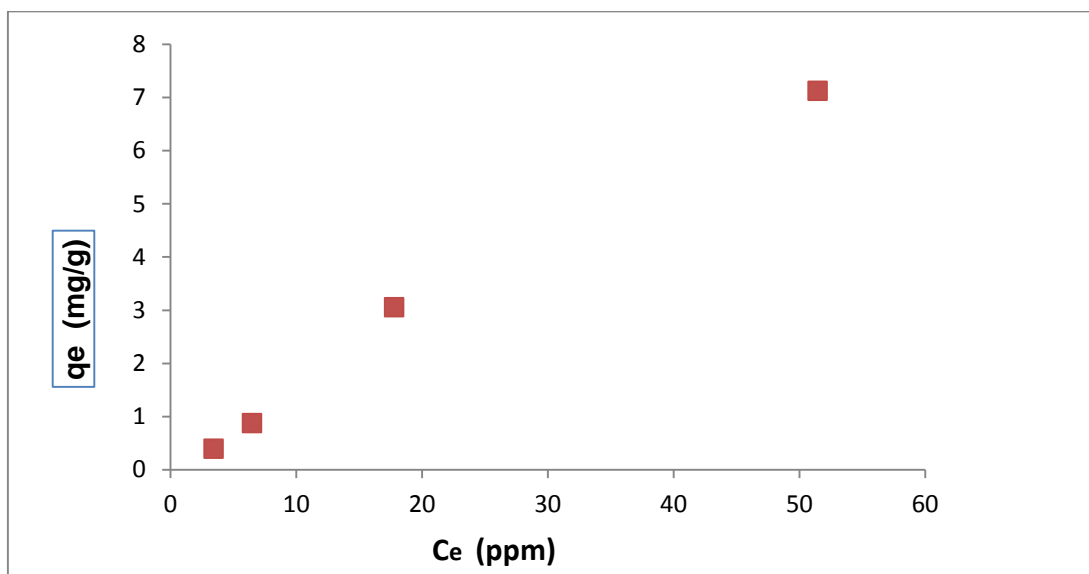
**Table (3. 5): Isotherms constants for Cd(II) adsorption onto AAC**

Langmuir` Isotherm			Freundlich` Isotherm		
$R^2$	$K_L$ (L/mg)	$Q_{max}$ (mg/g)	$R^2$	$K_F$ $((\text{mg/g})(\text{L/mg})^{1/n})$	N
0.902	7.562	66.67	0.998	0.539	2.09

$R^2$  estimated numbers from Freundlich isotherm is suitable result with the data better than Langmuir`. The Freundlich` modeling shows that adsorption may occur due to electrostatic complexation between the investigated heavy metal ion and the bulk functional groups of activated carbon which is negatively charged and so adsorption occurred in multilayer system rather one layer.

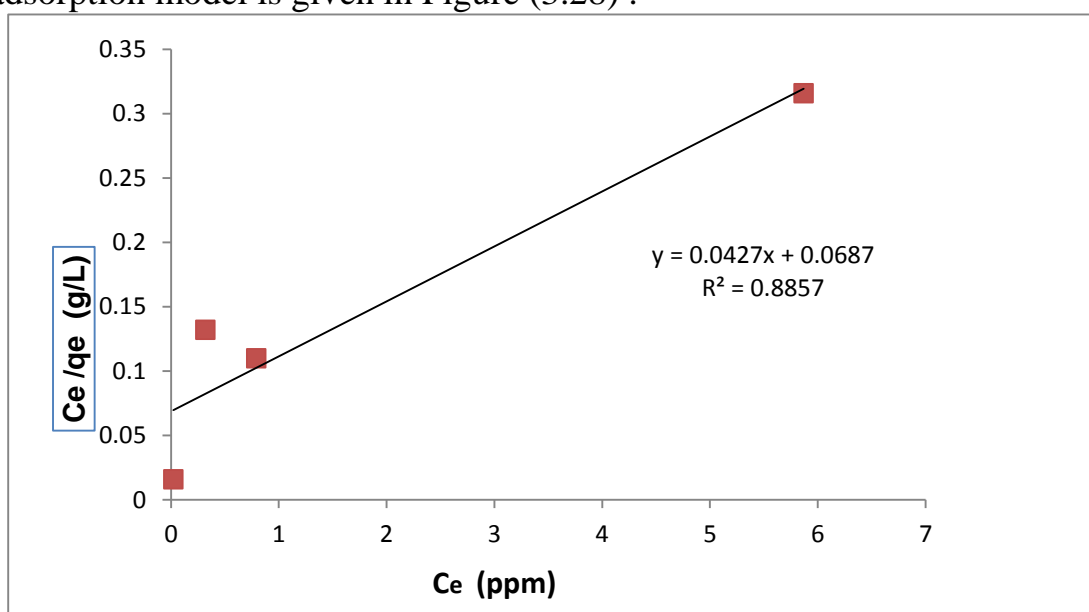
The adsorption was tended to fit Freundlich better as constant (n) placed in arrange of (1--10). Bigger value of n (smaller value of  $1/n$ ) indicated stronger interaction between the adsorbent and the adsorbate. From Table 3.5 (n) value was seen to place between (1 -10) range showing valuable adsorption of cadmium ion on the prepared activated carbon.

Langmuir` and Freundlich` modeling forms were used to characterized the adsorption-isotherm to study relationship between the amounts of lead adsorbed ( $q_e$ ) and its equilibrium concentration in solution onto AAC ( $C_e$ ) is given in Figure (3.27-3.29):



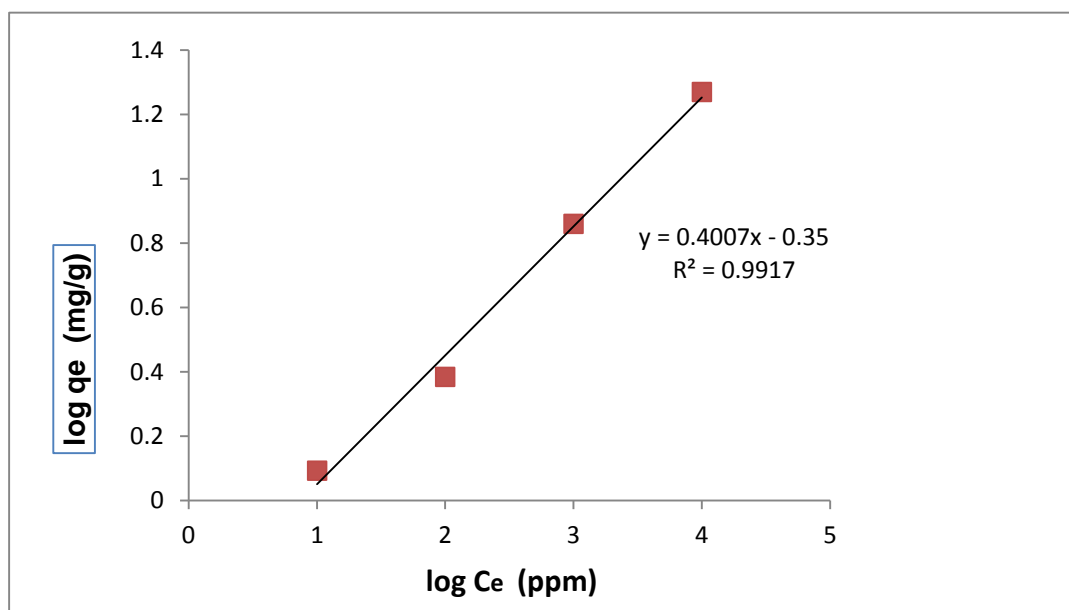
**Figure (3. 27):** adsorption-isotherm at equilibrium state of pb(II) onto AAC at (temperature;; 25 oC, initial pH 4 , after 7hr and solid:: liquid ratio 0.2 g::50 mL)

Adsorption isotherm for lead onto AAC at 25 °C using Langmuir adsorption model is given in Figure (3.28) :



**Figure (3. 28):** Plotting of Langmuir` for pb(II) adsorption onto AAC (temperature;; 25 o C, initial pH;; 4 and solid:: liquid ratio 0.2g ::50 mL)

Adsorption isotherm for lead onto AAC at 25 °C using Freundlich adsorption model is given in Figure (3.29) :



**Figure (3. 29):** Plotting of Freundlich's plot for pb(II) adsorption onto AAC (temperature;; 25 ° C, initial pH;; 4 and solid:: liquid ratio: 0.2 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 (3.6) :

**Table (3. 6): Isotherms constants for pb(II) adsorption onto AAC**

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
0.885	0.068	23.8	0.991	0.446	2.5

$R^2$  estimated numbers from Freundlich isotherm is suitable result with the data better than Langmuir'. The Freundlich' modeling shows that adsorption may occur due to electrostatic complexation between the investigated heavy metal ion and the bulk functional groups of activated



carbon which is negatively charged and so adsorption occurred in multilayer system rather one layer.

The adsorption was tended to fit Freundlich better as constant (n) placed in arrange of (1--10). Bigger value of n (smaller value of  $1/n$ ) indicated stronger interaction between the adsorbent and the adsorbate. From Table 3.6 (n) value was seen to place between (1 -10) range showing valuable adsorption of cadmium ion on the prepared activated carbon.

It was obvious that fitting occurred well in the experimental data results and Freundlich model . as the investigated metal ions adsorbed had coefficient of determination  $R^2 > 0.9$ . This showed that the Freundlich isotherm was a best choice for multiple adsorption of the investigated heavy metals using activated carbon from *Asphodelus ramosus* tuber . Similar results were reported when Freundlich model was the best describing model for the Sorption's process of lead, Nickle , copper and Cadmium from the tested aqueous-solution by stone wastes from olive tree [90].

Resulted numbers of  $1/n$ , below unity indicated favorable adsorbing mechanism will take place at low metal concentration but the increasing in the quantity adsorbed will be less at larger values of concentration [91].

**Conclusion and Recommendations :**

good results were obtained from this project these results include:

1. many advantages were obtained from using this prepared activated carbon as cheap, simple and efficient source for heavy metal elimination from waste water even with low metal ions concentrations.
2. More investigations for this plant tubers extracts must be performed in future to show more therapeutic effects of this medicinal plant.
3. Characterizations for AAC must be performed in more advanced methods.
4. Phytochemical composition of the tuber extracts must be characterized using more advanced method.
5. Quantitative determination of some phytochemicals must be done in-vitro for this tuber extracts.
6. It seems by applying iodine number method for surface area determination that the highest surface area was 506.5m<sup>2</sup>/g when precursor was activated using ZnCL<sub>2</sub>.
7. The ideal pH in adsorption process was equal 12 for all heavy metal ions as at alkaline pH the activated carbon functional groups were negatively charged and can be able to interact with every tested heavy metals cation.
8. It was better to remove heavy metals ions from aqueous solution at high temperature as 45°C as these ions freely moving toward activated carbon and interact with its functional groups at higher temperature.

9. Freundlich adsorption isotherm was the best equation that described removal of all investigated heavy metals.
10. Adsorption process equilibrium state in heavy metal removing from the tested solutions was occurred after 7hr for all heavy metal ions

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جامعة النجاح الوطنية

كلية الدراسات العليا

دراسة مقارنة بين الفحم التجاري والفحم المستخلص  
من ابصال نبات البروق المتفرع في ازالة المعادن  
الثقيلة من محلول مائي

إعداد

عبد الله محاميد

إشراف

د. أحمد أبو عبيد

د. نضال جرادات

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم البيئية  
بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2017



ب

دراسة مقارنة بين الفحم التجاري والفحم المستخلص من ابصال نبات البروق المتفرع في ازالة المعادن الثقيلة من محلول مائي.

اعداد

عبدالله محاميد

اشراف

د.أحمد ابو عبيد

د.نضال جرادات

### الملخص

يعتبر هذا البحث من احدى المشاريع العلمية التي تهدف الى استخلاص مركبات طبيعية من درنات نبات البروق المتفرع باستخدام مذيبات مختلفة القطبية مثل الهكسان والأسيتون والميثانول والماء المقطر وتطبيق مجموعة من الفحوصات المخبرية لمعرفة التأثيرات الطبية لهذه المركبات. وقد تم ملاحظة أن المستخلص الميثانولي هو اغنى الأنواع الأربعة بالمركبات الحيوية حيث ظهر أنه الأكثر احتواء على المركبات الفينولية المضادة للأكسدة والفلافونيد ومركبات الجلايكوسيد التي تعتبر من أكثر النواتج الطبيعية استخداما في الطب كما أنه يحتوي على المركبات القابضة ( التانين) والمركبات القلوية.

وتم تدعيم هذه النتيجة باظهار تأثيره المضاد للأكسدة على أنه الأفضل مقارنة بالأنواع الأخرى كما أنه كان الأفضل في تأثيره على أنزيم اللايباز وبالتالي منع امتصاص الدهون الموجودة في وجبات الطعام وبالتالي قد تكون له فائدة طبية بالمستقبل كعلاج طبيعي للسمنة كما تم في هذا البحث تحضير كربون منشط من أنسجة درنات البروق المتفرع بعد حرقها وتحويلها الى رماد، وتم اتباع خطوات التنشيط بكلا الطريقتين الفيزيائي والكيميائي وظهر أن استخدام كلوريد الزنك كمنشط كيميائي قد أنتج أعلى مساحه سطح للكربون المنشط الناتج والتي تم تققيمها من خلال فحص معايير ذرات اليود.وبعد ذلك تم عمل دراسة مقارنة بين الكربون المنشط التجاري والكربون الذي تم انتاجه من درنات البروق المتفرع في ازاله أربعه أنواع من أيونات العناصر الثقيلة مثل أيونات الكروميوم والكادميوم والرصاص والنحاس . ودراسه مدى تأثير بعض العوامل

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كالوقت والرقم الهيدروجيني ودرجه الحرارة وتركيز العناصر الثقيلة على نسبة الازالة من المحلول المائي المحتوي على أيونات هذه العناصر الثقيلة.

زمن خلال هذه الدراسة ظهر أن الوسط القاعدي هو الأفضل لعملية ارتباط هذه الأيونات بسطح الكربون المنشط وان درجات الحرارة العالية تزيد من نسبة الازاله كما أن الاتزان يحدث بعد 7 ساعات من عملية التحريك.وبعد تطبيق معادلتى adsorption isotherm تم ايجاد أن جميع العناصر الثقيلة المدروسة تتبع لمعادلة Freundlich التي من خلالها يتم ارتباط الأيونات الموجبه للعناصر الثقيلة مع الأسطح ذات الشحنة السالبة للكربون المنشط وتتم العملية على عدة طبقات .