بسم الله الرحمن الرحيم

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College of Science

Department of Chemistry

REMOVAL OF SOME TOXIC CONSTITUENTS FROM WATER BY GRAPHITIC CARBON NANOTUBES

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

By

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المستخلص:

تشكل الكلفة العالية لتحضير أنابيب الكربون النانوية تحديا كبيرا يواجه صناعة وتطبيقات هذه المادة المهمة في الانتاج الصناعي والتطبيقات الحياتية. تم تحضير ستة عينات من أنابيب الكربون الجرافيتة على أسطوانة من الحديد المقاوم للصداء بطريقة الترسيب الكيميائي البخاري. تم تحليل مكونات العينات بواسطة جهاز الأشعة السينية الناشر للطاقة (EDX) ، كما تم تصويرها بالمجهر الألكتروني الماسح (SEM) والمجهر الالكتروني النفقي (TEM) الذي أظهر ان متوسط سمكها يساوي ٩٣,١١ نانومتر. أستعملت العينات الستة كمواد مازة لصبغة الملاكايت الاخضر من عينة مياه محضرة معمليا في الظلام والضوء المرئي . أعطت العينات الستة كفاءة أزلة كالتالي :

٢٤٩,٤٣ ، ٢٤٩,٠٨، ٢٤٧,٨٠، ٢٤٨,٦٢ ،٢٤٩,٦٥، و ٢٤٤,٦٢ ملليقرام / جرام في الظلام بعد ٧٠ دقيقة . كما أظهرت كفاءة إزالة كالتالي عندما تم الامتزاز في الضوء المرئي ٢٤٨,٧٨ ، ٢٤٧,٦٨، ٢٤٥,٠٢، ٢٤٧,١٦، ٢٤٨,٢٣، ٢٤٧,٦١ ملليقرام / جرام بعد ١٣٠ دقيقة .

Abstract:

The challenge of high cost of carbon nanotubes, CNT, synthesis is a major obstacle facing the mass production and industrialized applications of this fascinating new material. Six Graphitic Carbon Nanotubes (GCNTs) were successfully prepared on commercial stainless steel cylinder by catalytic chemical vapor deposition method using ethyl alcohol as a carbon source. Characterization of the samples by EDX, SEM and TEM which confirmed the presence of thick wall GCNTs of 93.11 nm average diameter . The samples were used to adsorb malachite green dye in the dark and visible light from synthetic water sample and all sample showed excellent removal efficiency. The samples showed removal efficiency of 249.43, 249.08, 247.80, 248.62, 249.65 and 244.62 mg/g for GCNT1, GCNT2, GCNT3, GCNT4, GCNT5 and GCNT6 respectively for the dye in the dark at 70 minutes contact time. The equilibrium time for the maximum removal efficiency in the visible light was longer (130 minutes) and the removal efficiencies are 248.78, 247.68, 245.02, 247.16, 248.23 and 247.61 mg/g respectively.

CHAPTER ONE

1. Introduction:

1.1. Carbon

Carbon (C_6^{12}) is the sixth element in the periodic table that provides the basis for life on Earth during photosthynesis process carried by plant and algae. It has many technological applications, ranging from drugs to synthetic materials.

Millions of organic and inorganic compounds in which carbon is a major element were discovered. This role is a consequence of carbon's ability to bind to itself and to nearly all elements in almost limitless variety. The difference in the structure of the molecules including carbon , results in diverse chemical and physical properties. [1].

1.2. Carbon Allotropes

Elemental carbon exists in two natural allotropes, diamond and graphite, which consist of extended networks of *sp*3- and *sp*2 -hybridized carbon atoms, respectively. Both forms show unique physical properties such as hardness, thermal conductivity, lubrication behavior or electrical conductivity. Conceptually, many other ways to construct carbon allotropes are possible by altering the periodic binding sequences in networks consisting of *sp*3-, *sp*2-and *sp*-hybridized carbon atoms. Recently, many synthetic carbon allotropes were synthesized and discovered such as fullerenes, graphene, carbon nanotubes, carbon 60 and carbon70, resulting in a recent scientific research trend to establish a family of synthetic carbon allotropes. [2]

1.3. Objectives of the study

The objective of this research is to prepare and characterize graphitic carbon nanotubes (GCNTs) and to estimate its efficiency for adsorption of malachite green dye in water as a measure of organic pollutants removal from waste water.

CHAPTER TWO
LITERATURE REVEIW

2.1. Natural Carbon Allotropes

Graphite and diamond are the two natural mineral forms of carbon. Diamond formed in the mantle of the earth under extreme heat and pressure. Most graphite found near Earth's surface and was formed within the crust at lower temperatures and pressures. Graphite and diamond share the same composition but have very different structures.

The carbon atoms in graphite are linked in a hexagonal network which forms sheets that are one atom thick. These sheets are poorly connected and easily cleave or slide over one another if subjected to a small amount of force. This gives graphite its very low hardness, its perfect cleavage, and its slippery feeling.

In contrast, the carbon atoms in diamond are linked into a frameworks structure. Every carbon atom is linked into a three-dimensional network with four other carbon atoms with strong covalent bonds. This arrangement holds the atoms firmly in place and makes diamond an exceptionally hard material. **[3]**.

2.1.1. Natural Graphite

Natural Graphite is a mineral consisting of graphitic carbon. It varies considerably in crystallinity. Most commercial (natural) graphites are mined and often contain other minerals. Subsequent to mining the graphite often requires a considerable amount of mineral processing such as froth flotation to concentrate the graphite. Natural graphite is an excellent conductor of heat and electricity. It is stable over a wide range of temperatures. Graphite is a highly refractory material with a high melting point (3650°C.) Natural graphite is subdivided into three types of material; Amorphous, Flake and High Crystalline graphite. **[3]**

2.1.2. Diamond

The carbon atoms in diamond are linked into a frameworks structure. Every carbon atom is linked into a three-dimensional network with four other carbon atoms with strong covalent bonds. This arrangement holds the atoms firmly in place and makes diamond an exceptionally hard material **[3].**

2.2. Synthetic Carbon Allotropes

The preparation of synthetic carbon allotropes started in 1985, with the advent of fullerenes , which were observed for the first time by Kroto and coworkers. The fullerenes, of which the smallest stable and most prominent is C60, are molecular carbon allotropes. C60 consists of a spherical network of sixty structurally equivalent sp^2-hybridized carbon atoms in the shape of a football , composed of 12 pentagons and 20 hexagons. Many representatives of higher fullerenes such as C70, C76, C84 and more recently C90 have been isolated and structurally characterized.

This discovery marked the beginning of an era of synthetic carbon allotropes. Now, the growing family of synthetic carbon allotropes, which includes the synthesis of carbon nanotubes in 1991 and the rediscovery of graphene in 2004. **[4]**

The quasi-one-dimensional carbon nanotubes are prepared out of evaporated graphite was reported. Later, a series of alternative production methods for carbon nanotubes, such as chemical vapour deposition methods, were developed. Depending on the preparation conditions, either singlewalled or multiwalled carbon nanotubes are obtained. The youngest synthetic carbon allotrope is two-dimensional graphene, representing a single graphite sheet. Graphene, the ultimate example of expanded aromatic carbon, was considered for a very long time to be an exclusively theoretical material. Recently, however, single graphene layers were prepared successfully by means of a simple mechanical exfoliation of graphite . Of the three families of carbon allotropes, graphene is the most structurally uniform material where only the sheet extensions and nature of edges can differ. [**2**]

2.3. Carbon Nanomaterials and waste water treatment

Nanoscience and Nanotechnology suggest that many of the current problems involving water quality can be solved or greatly ameliorated using the nanoscale adsorbents, called nanoadsorbents. Innovations in the development of novel carbon nanomaterials like fullerenes, carbon nanotubes, and graphene are among the most exciting and promising materials for water treatment and purification.

The nanomaterials, particularly carbon nanostructures, are promising systems for several applications, in particular for molecule adsorption due to their intrinsic dimensionality, textural, and electronic properties. The carbon allotropes differ in the coordination number of the carbon atoms or in the packaging sequence of the layers in the crystal lattice environment. Different

degrees of sp^2 hybridization result in carbonaceous nanomaterials with distinct atomic bonds and arrangements. For example, a two dimension, 2D, carbon allotropic form, such as graphene, is a hypothetical infinite aromatic surface with sp^2 hybridization and a carbon atom thickness. The structure of single-walled (SWCNT) and multiwalled carbon nanotubes (MWCNT) , both 1D systems, can be simplified as the result of one or more graphene sheets rolled up in a concentric form, respectively. On the other hand, a 0D system such as fullerene, C60, consists of 60 carbon atoms with sp^2-like hybridization with 20 hexagonal and 12 pentagonal rings, which are responsible for its curvature . These topological changes provide different interactions between carbon-based nanoadsorbents and the adsorbate molecule . Apart from fullerene, carbon nanotubes, and graphene family in isolated form, it should be also taken into account those materials when available in 3D arrangements (bulk) . Figure 1, presents some examples for 0D, 1D, 2D, and 3D carbon nanostructures. The union of several isolated carbon structures can change the behavior of adsorption process because when they are in clusters form they present new unit adsorption sites. [5]

0D	1D	2D	3D
Fullerene	Carbon Nanotube	Graphene	Graphite
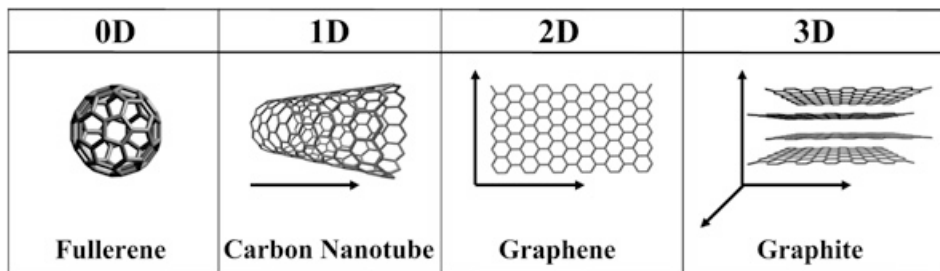
Fig. 1: some examples for 0D, 1D, 2D, and 3D carbon nanostructures.

2.4. Synthetic Graphite

"Synthetic graphite" is made by heating high-carbon materials like petroleum coke and coal-tar pitch to temperatures in the range of 2500 to 3000 degrees Celsius. At these high temperatures, all volatile materials and many metals in the feedstock are destroyed or driven off. The graphite that remains links into a sheet-like crystalline structure. Synthetic graphite can have a purity of over 99% carbon, and it is used in manufactured products where an extremely pure material is require. [6]

Graphite is a valuable industrial mateial, it enters in many industries and technological applications such as Refractory Materials, Chemical Industry, Nuclear Industry. Electrical Applications, Mechanical Applications. [7]

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2.5. Carbon Nanotubes

Carbon nanotubes, CNTs, can be considered as seamless, rolled-up graphite sheets. Two types of CNTs can be prepared, singlewalled CNT or multiwalled CNTs according to the number of the concentric tubes. These tubular networks of bent sp^2-hybridized atoms are characterized by a pronounced one-dimensionality because of a very high aspect ratio (length/ diameter ratio); typical diameters of single-walled carbon nanotubes are around one to two nanometers, but their lengths can easily reach millimeters and above. Present production methods of carbon nanotubes lead to the formation of mixtures consisting of tubes with many different helicities, characterized by so so-called *m,n*-values of the role up vectors. [8]

2.6. Synthesis of Carbon Nanotubes

CNT can be prepared through many physical and chemical methods. The methods frequently applied are Arc-discharge, Laser ablation and Chemical vapor deposition methods, below is the broad outlines of each method.

2.6.1. Arc-discharge method

In this method, graphite electrodes are evaporated in an electric arc of high voltage at very high temperature of about 4000 ^{0}C. The carbon of the graphite electrodes rolled in a form of MWCNTs. Through this method, Iijima discovered and characterized the MWCNTs for the first time in 1991. The MWCNTs produced are well crystalline but they are highly impure. [9]

2.6.2. Laser ablation method

Application of high power laser in high temperature furnaces evaporate pure graphite to form CNT of high purity but of very low yield. [9]

2.6.3. Chemical vapor deposition method (CVD)

Chemical Vapor Deposition (CVD) or Catalytic Chemical Vapor Deposition (CCVD) is the most widely used method for synthesis of CNT due to its simplicity , the capability to control the decomposition parameters to produce the desired type of CNT and the potential to scaling up for industrial production. The CVD method involve the passage of the vapor of an organic precursor on or with a catalyst in a hot cylindrical tube furnace (600 -1200 ^{0}C) for a certain period of time between 15 to 60 minutes. [8,9]

2.7. carbon precursors in CVD method

Pure and homogenous organic materials are commonly used as organic substrates for the production of CNT such as acetylene, methane, ethylene, benzene, xylene , carbon monoxide, cyclohexane, fullerene ... etc. Highly pure SWCNTs were frequently produced from mono or di-carbon atom precursor such as carbon monoxide, methane, acetylene and ethanol in addition to many others using the appropriate catalysts. The carbon precursor can be supplied to the reactor in the gas phase such as carbon monoxide, acetylene and methane. **[8, 9].**

2.8. Purification of CNT

As-produced carbon nanotubes are intrinsically inert, and may contain impurities such as amorphous carbon or catalytic metal particles. The purification processes that have been investigated usually utilize the differences in the aspect ratio and oxidation rate between the CNTs and impurities . A post-synthesis treatment is almost always required to purify and disperse the CNTs in a suitable solvent; a wide variety of approaches have been developed. A typical strategy is to use thermal oxidation, then acid reflux in concentrated HCl, and finally a thermal annealing treatment to purify the raw material; a surfactant can subsequently be used to disperse the CNTs using sonication .. Alternatively, a mixture of concentrated nitric and sulphuric acids can simultaneously purify, shorten and functionalize CNTs .**[8]**

2.9. Properties of CNT

The electronic properties of CNT as a conductor or a semiconductor depends largely upon their geometrical characteristics, so they are incorporated in many devices such as electronic circuits, field emission devices. The thermal properties of CNT are outstanding exceeding that of copper metal. Their mechanical properties dominate that of steel with several orders of magnitude, this property renders CNTs as strongest fiber ever known till date. CNT were used in many useful applications replacing the ordinary materials with successful results. Examples of these applications are applications in fields such as water treatment, electron field emission, sensors, probing tips, lithium batteries hydrogen storage and mechanical reinforcements as composite filling due to their high tensile strength and low density **[10].**

2.10.Characterization of CNT

Electron microscopy is an imaging technique that uses an electron beam in order to scan the topography of the material. Since the wavelength of an electron is much smaller than the wavelength of visible light, diffraction effects occur at much smaller physical dimensions. The microscope was the first tool by means of which a real study could be made of objects too small to be seen with the naked eye. The best characterization tools for the nanomaterials in general and the carbon nanotubes in particular are the transmission electron microscope TEM, scanning electron microscope SEM, energy dispersive X- ray , EDX, thermogravimetric analysis , TGA, and X-ray diffraction, XRD, in addition to many other techniques. **[8, 9]**

2.11. Applications of CNT

CNT gain an exciting properties that make it a wonder between other materials. Among these properties is that it is 100 times stronger than steel and six times lighter than it, harder and more heat resisting than diamond, electrical conductance thousand times more than copper and can be a semiconductor ,high thermal stability up to 4000 ^{0}C, in addition to high surface area and the ability to chemical functionalization. According to these unusual properties, many applications of CNT were now proposed to replace the ordinary bulk materials. CNT can be applied as reinforcing materials for many composites, in nano electronic circuits, optical uses, biomedicine, biosensor and many other applications . **[11].**

2.12. Adsorption

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface. The term also refers to a method of treating wastes in which activated carbon is used to remove organic compounds from wastewater. **[12]**

Types of Adsorption

There are two types of adsorption phenomena, physical and chemical. These two types of adsorption depend on the nature of the attractive forces involved. Molecules may be concentrated at interfaces by only one type of attraction force, many adsorption process involve more than one type of attraction forces operating together.

Physical Adsorption

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed. For example , the intermolecular attractive forces between a solid and gas are greater than those existing between molecules of gas itself ,the gas will condense upon the surface of the solid even though its pressure may be lower than the vapor pressure corresponding to prevailing temperature. **[13].**

The adsorbed substance does not penetrate within the crystal lattice of the solid and does not dissolve in it but remains entirely upon the. If the solid is highly porous and containing many fine capillaries, the adsorbed substance will penetrate these interstices if it wets the solid.

Chemisorption, or Activated Adsorption

Chemisorption, or activated adsorption, results of chemical interaction between the solid and adsorbed substance . It is always accompanied by chemical reaction. The process is frequently irreversible, and on desorption the original substance will often be found to have undergone a chemical change. Chemisorption may occur at each of the five types of an interfaces "solid-solid, solid-gas, solid-liquid, liquid-liquid, and liquid-gas" but solid-gas and solid-liquid are the most important. A chemically adsorbed gas or liquid is usually very difficult to remove. The process of dyeing is the form of chemical adsorption. **[13]**

2.13. Carbon Adsorption

Carbon adsorption is a remediation technology that removes contaminants from air or water through physical adsorption into the carbon grain. Carbon is "activated" to improve adsorption through a process that creates porous particles that have large internal surface areas. A number of commercial grades of activated carbon are available such as, bone char is obtained from the destructive distillation of crushed, dried bones at temperature in the range (600 to 900 C^0). It is used chiefly in the refining of sugar and can be reused after washing and burning. Decolorizing carbons are used for a great variety of purposes, including the decolorizing of solution of sugar, industrial chemical, drugs, dry cleaning liquids, water purification, refining of vegetable and animal oils, and in recovery of gold and silver from cyanide ore-leash solutions. Gas adsorbents available in granular or pellet form and is used for recovery of solvent vapors from gas mixtures , gas masks,

collection of gasoline hydrocarbons form natural gas and the fractionation of hydrocarbon gases. It is revivified for reuse by evaporation of the adsorbed gas. **[14]**

2.14. Malachite Green

Malachite green is an organic dye of highly cytotoxic to mammalian cells and also acts as a liver tumor enhancing agent. The concentration and effective utilization of activated carbon generated from natural plant material have attracted worldwide attention in a view of the large disposal problem in the environment. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, *etc*., as carbonaceous precursors for the removal of dyes from water and wastewater. **[15,16].** The lethal dose of malachite green (LD50%) is 80 mg/kg for rats and it is suspected to cause carcinogenic symptoms.
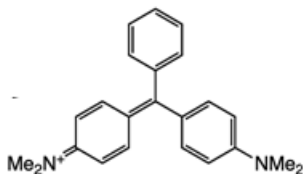
2.15. Treatment of Waste Water with Carbon Materials

Adsorption is typically used in wastewater treatment to remove toxic organic pollutants and to a lesser extent, inorganic contaminants, from the wastewater. Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge. Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment . In any adsorption process the material being adsorbed (e.g., a pollutant) is simply but effectively removed from one phase (e.g., a wastewater) and transferred to another phase (e.g., activated carbon).· This means that adsorption is a physical separation process in which the adsorbed material is not chemically altered**.[4]**

Waste water discharge from domestic, industrial or agricultural sources encompasses a wide range of contaminants and has drawn major concern worldwide since they adversely affect the quality of water. Removal of these contaminants relies on the sorption behavior of a sorbent. CNTs, with their high surface active site to volume ratio and controlled pore size distribution, have an exceptional sorption capability and high sorption efficiency compared to conventional granular and powder activated carbon, which have intrinsic limitations like surface active sites and the activation

energy of sorption. Extensively studies found that the adsorption capacity of CNTs depends on both the surface functional groups and the nature of the sorbate. Forinstance, the amounts of surface acidity (carboxylic, lactonic and phenolic groups) favor the adsorption of polar compounds.On the other hand, the unfunctionalized CNTs surface is proved to have higher adsorption capacity towards non-polar compounds such as polycyclic aromatic hydrocarbons.The sorption behaviors of CNTs mainly involve chemical interaction for polar compounds and physical interaction for non-polar compounds. The sorption of both polar and non-polar compounds is normally fitted with Langmuir or Freundlich isotherms. **[17,18]**

CHAPTER THREE

MATERIALS AND METHODS

3.1. Synthesis of graphitic GCNT by Catalytic Chemical Vapor Deposition (CCVD)

The catalytic Chemical Vapor Deposition (CVD) technique was followed in the preparation of 6 samples of graphitic carbon nanotubes (GCNT) as a soot byproduct during the preparation of CNT on different metal oxides catalysts. The GCNT was deposited as a black soot on the inner surface of the stainless cylinder in the tubular furnace reactor made of heater and stainless steel cylinder of 800 mm in length and 40 mm inner diameter **[9]**. The experiment was carried as follows; 40 liter/hour nitrogen gas current was allowed to flow through the cylinder while the temperature of the furnace was increased gradually at a rate of 20 ^{0}C/minute to the reaction temperature at 700 ^{0}C. When the temperature reached about 550^0C, the 500 ml Pyrex glass conical flask containing 40 ml of pure ethanol was heated to boil gradually on a hotplate, when the temperature of the furnace reached 700 ^{0}C, the ethanol vapor was carried by the current of the nitrogen gas to the reaction zone in the SS cylinder at a rate of 2 ml of/minute. All the 40 ml of ethanol were evaporated in about 20 minutes and entered to the reaction zone to grew the GCNT on the surface of the cylinder. The exhaust joint was attached to the SS cylinder and connected to the fume hood. After all ethanol evaporated, the reaction was allowed at 700 ^{0}C for further 20 minutes, the ethanol vapor valve was closed and the empty flask was removed and the reaction temperature started to decrease gradually under the nitrogen gas current until it reached 250 ^{0}C, then the nitrogen flow was stopped and the cylinder and its content were allowed to cool to the room temp. The cylinder and its content were removed from the furnace the black graphitic CNTs were removed in a plastic container.
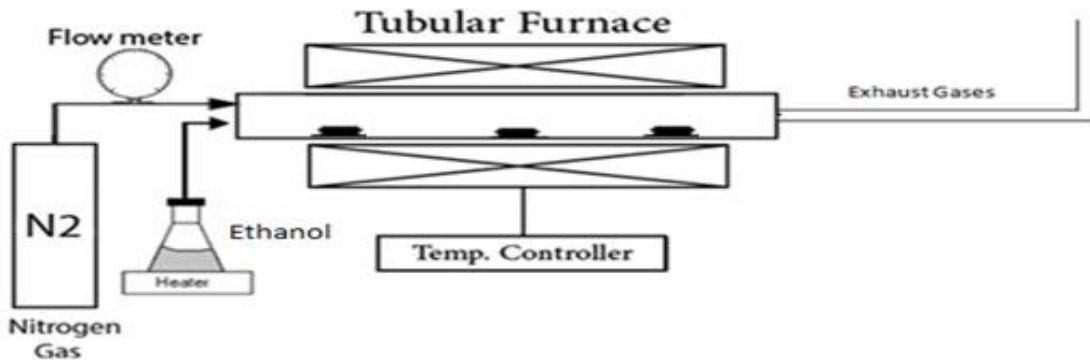

Fig. 2: Schematic diagram of chemical vapor deposition reactor used.

3.2 . Purification of GCNT

The crude GCNTs were purified by boiling in a mixture of 30 ml of concentrated hydrochloric acid and 10 ml of conc. nitric acid for 30 minutes, allowed to stay for 24 hours then filtered under suction using Buchner apparatus . The filter paper was washed with distilled water until free of the acid, then dried at 80 ^{0}C for 6 hours in the oven, collected and preserved in plastic container for further characterization.

3.3. Characterization of graphitic GCNT by EDX, SEM and TEM

The composition and morphology of GCNTs was estimated using Scanning Electron -Energy Dispersive X- Ray technique (SEM-EDX) model JSM-IT300 - scanning electron microscope. Table 1 showed the composition obtained by EDX. The morphology of four samples of GCNTs was characterized by scanning electron microscopy SEM , the results were shown in fig. 3. GCNT1 was imaged using transmission electron microscopy (TEM) model JEOL-1011 , Electron Microscope, the results were shown in fig. 4.

3.4. Adsorption of Malachite Green (MG) on GCNTs in the dark

50 ml of 250 mg/L MG solution were added to 50 mg of sample 1,2,3,4,5 and 6 in 50 ml Erlenmeyer flask, the PH of the solution was adjusted to 9 using diluted sodium hydroxide and hydrochloric acid solutions. The mixtures were magnetically stirred at 500 rpm in the dark by covering the magnetic stirrer and the reaction flasks with opaque box. Every 10 min interval , about 6ml of the suspensions were withdrawn and filtered on filter paper and the absorbance of the clear solution was read immediately on a UV-VIS spectrophotometer model spectro UV-VIS double beam –UV D3500 LABOMED incorporation at λ_{max} 616 nm and the absorbance were recorded . The adsorption efficiency of the six samples was determined on a calibration curve of 0-5-10-20-40-60-100 mg/l of MG.

3.5. Adsorption of malachite green (MG) on the GCNTs samples in the visible light

The same procedure followed for the treatment of malachite green with graphitic carbon nanotubes in the dark were followed for the visible light treatment, except that the time intervals were increased to 20 minutes and the adsorption time was extended to 150 minutes and a calibration curve of 0-2.5-5-10-20-30 and-40 mg/L of MG was used.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Synthesis and purification of Graphitic carbon nanotubes GCNTs

 Six samples of GCNTs were successfully prepared as byproduct by chemical vapor deposition method on the bulk surface of the steel cylinder used in the reactor. The main goal of the experiments was to prepare pure CNTs on transition metal oxides nano particles in a porcelain boat. The GCNTs were deposited on the inner stainless steel surface of the cylinder as a black soot of about 2.0 grams mass for each sample. The crude GCNTs were scratched from the cylinder and purified using a mixture of hydrochloric and nitric acid in 3:1 volume ratio to remove metallic impurities of the steel components. Although, the production of CNT on the etched stainless steel sheets was reported in the literature **[9]** , the preparation of GCNT on untreated stainless steel was not mentioned. It is well known that the size of the catalyst used, determine the size of the CNT produced and the size of the CNT determine its properties and uses. Thick multiwalled graphitic carbon nanotubes were prepared in this research which may find new applications and uses in the field of technology.

Ethanol was used as carbon precursor for the production of GCNT, in all experiments , a black soot was observed on the catalyst in the boat and on the sides of the stainless steel cylinder, this may cause a contamination of MWCNT with appreciable quantities of undesired amorphous carbon and graphite which need a careful purification steps to yield reasonably pure GCNT to be characterized perfectly. The SEM and TEM images for some of the samples, showed that the CNT product is accompanied with graphitic material and amorphous carbon.

4.2. Characterization of GCNTs

4.2.1. EDX analysis

Sample 1,2,3 and 4 were analyzed using EDX technique interfaced to the SEM instrument used in the imaging of four samples. The data obtained showed that the purification step succeeded in removal of most metallic impurities from the carboneous product. Trace of impurities like iron and chromium from the stainless steel cylinder metals, chlorides from the acidic purification step and oxygen from air oxidation were expected . The results of EDX revealed that high carbon content

of sample 1 and 4 of more than 97.0 % was obtained by the acid purification and washing , the results were shown in table 1.

GCNT	Carbon%	Chloride%	Oxygen%	Iron %	Chromium%
GCNT1	97.85	0.47	0.00	0.81	0.87
GCNT2	92.74	1.01	6.24	0.00	0.00
GCNT3	85.11	0.93	13.73	0.23	0.00
GCNT4	97.54	2.00	0.00	0.00	0.47

Table 1: Elements percentage in GCNT1 ,2,3 and 4 using EDX.

4.2.2. SEM characterization of GCNTs

The scanning electron microscopy SEM for sample 1,2,3 and 4 , showed the images of thick GCNTs for all samples. The thick multiwalled GCNTs are highly surrounded by amorphous carbon and graphitic material. The GCNTs composite obtained can make benefits from the marvelous properties of both carbon nanotubes and graphitic carbon when making trails on application of the Thick multiwalled GCNTs.

Fig. 3, showed the images of four GCNTs samples. Thick GCNTs were clearly seen accompanied by graphitic and amorphous carbon embedded between the tubes **[19].** The presence of high amount of oxygen as impurity in sample 2 and 3 (table 1), yielded relatively clear carbon nanotubes, the ease of oxidation of graphite and amorphous carbon in comparison to difficult oxidation of CNTs, may be the reason for this behavior.
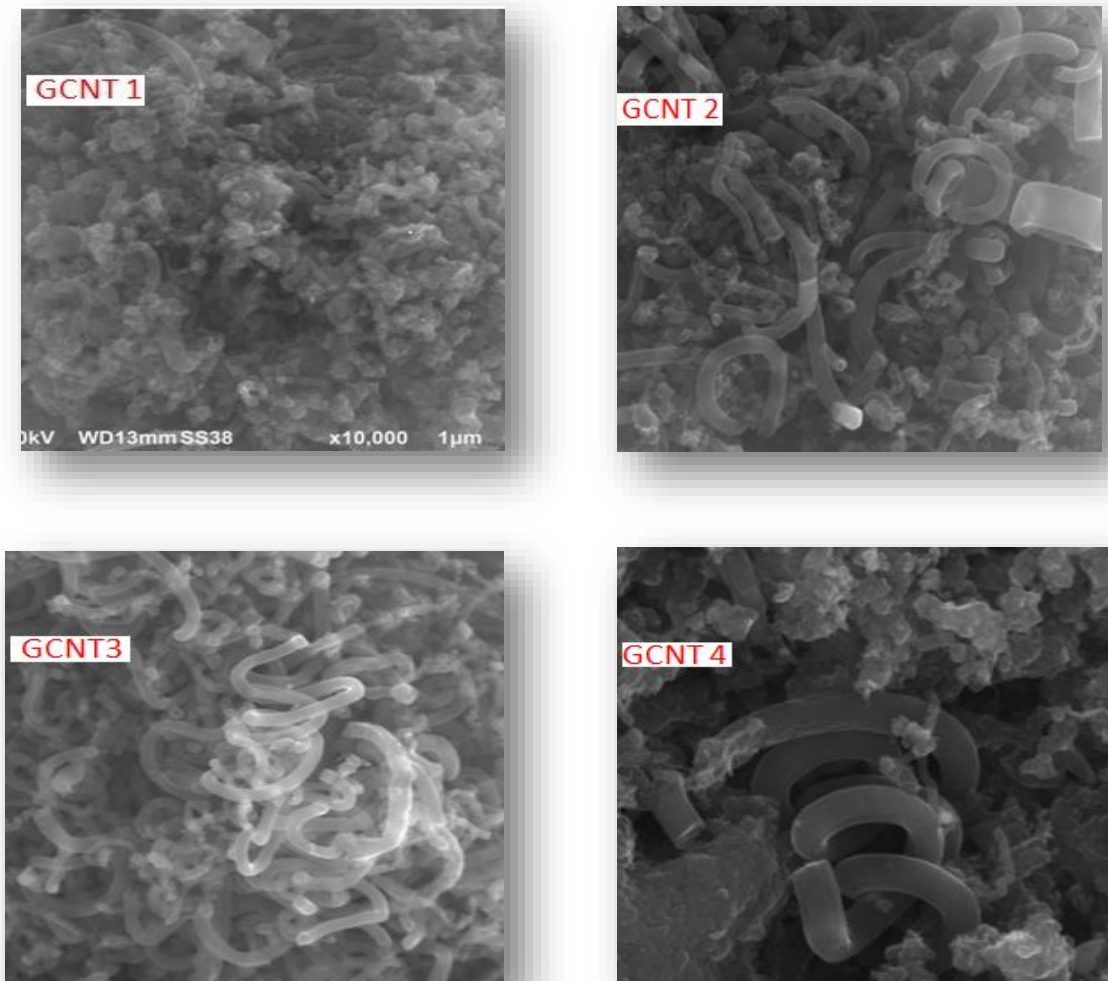
Fig.3: SEM images of GCNT 1,2,3 and 4 respectively at X10000, 1 micrometer scale.

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4.2.3. TEM characterization of GCNT1

Sample1, GCNT1, was scanned using TEM to estimate the average diameter of the thick GCNT obtained by the method adopted in the research. The average thickness was found to be 93.11 nm, Fig. 4a. The presence of graphitic and amorphous carboneous materials was confirmed in the images of Fig. 4b, c and d. The graphitic materials were found attached to the surface of thick wall GCNTs and even embedded between the concentric thick multi walls tubes. The thick walls of the GCNTs was noticed in the TEM image of Fig. 4e.
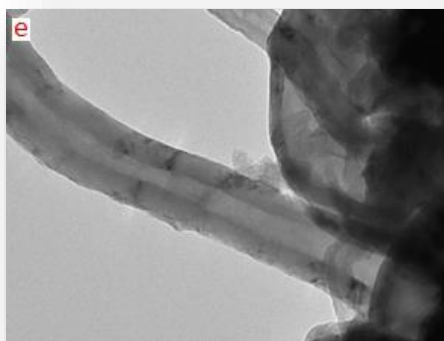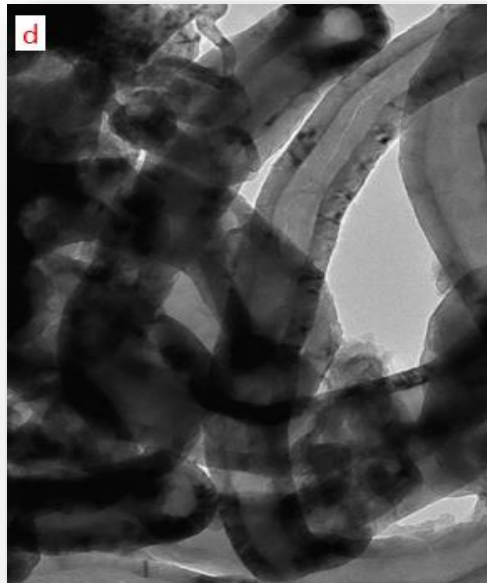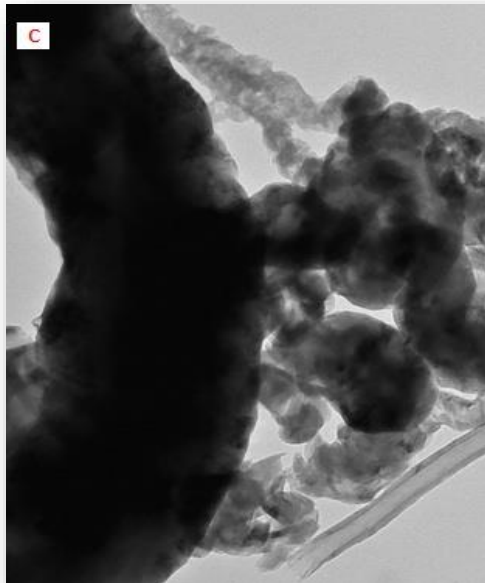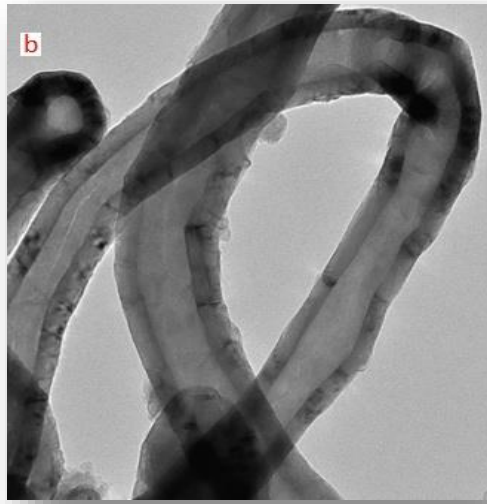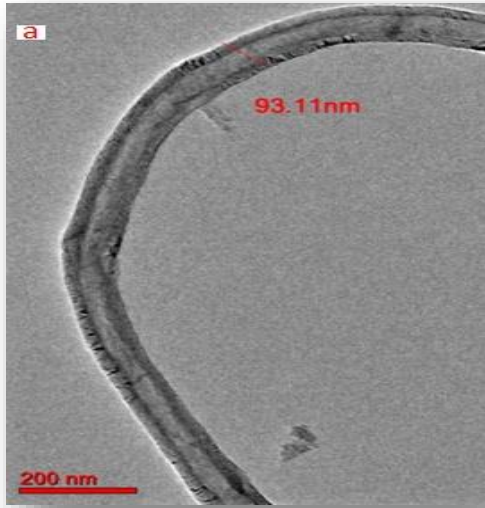
Fig. 4: TEM images of sample GCNT1 at X40000 and 200 and 100 nm scale.

4.3. Adsorption of Malachite Green on GCNTs in the dark

The calibration curve of malachite green (MG) used to calculate the adsorption efficiency was read at 616 nm wavelength and showed straight line with a linear equation of y= 0.0576 x + 0.1242 and a good correlation factor, R^2 = 0.9863. The concentration of the unadsorbed MG was calculated from the value of (x) at different absorbencies. The results were shown in table 2 and figure 5.

Table 2:Calibration curve of MG for the adsorption in the dark:

STD No.	STD Conc. in mg/l	Absorbance
1	5	0.394
2	10	0.7
3	20	1.474
4	40	2.32
5	60	3.27
6	80	4.97

Fig. 5: Calibration curve for MG adsorption on GCNTs in the dark.

The absorbance of the remaining MG solution was determined at 616 nm wavelength at different time periods at the interval of 10 minutes, the absorbance was recorded in table 3.

Table 3: Absorbance of MG adsorbed on 50 mg GCNTs (50 ml of 250 mg/l MG) in the dark:

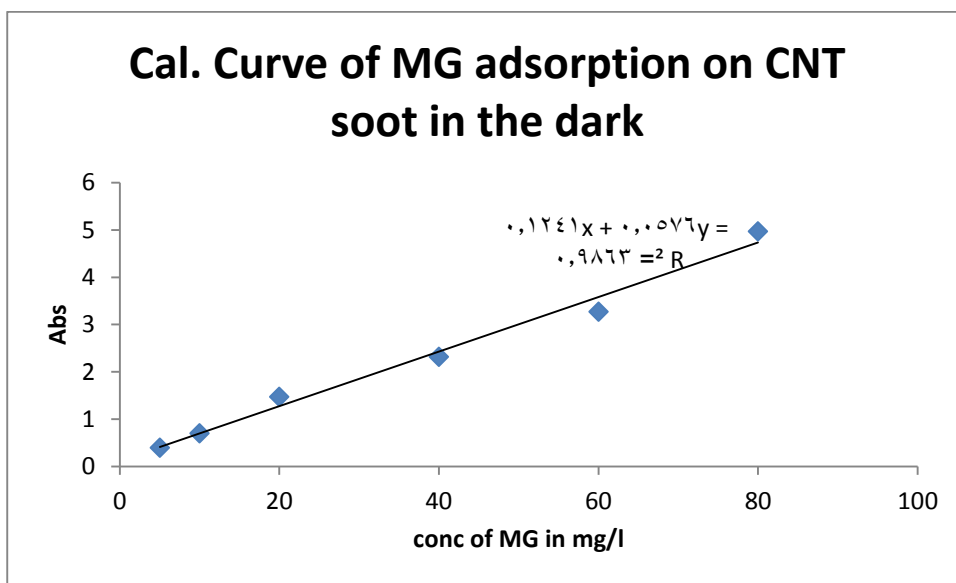| Sample No.	After 10 minutes	After 20 minutes	After 30 minutes	After 40 minutes	After 50 minutes	After 60 minutes	After 70 minutes	After 80 minutes
GCNT1	0.623	1.00	0.976	1.002	0.880	0.753	0.157	0.138
GCNT2	0.524	0.804	0.953	0.904	0.721	0.612	0.071	0.046
GCNT3	0.497	0.810	0.871	0.876	0.754	0.663	0.251	0.338
GCNT4	1.13	1.283	1.339	1.262	1.118	0.941	0.206	0.201
GCNT5	0.757	1.038	1.265	1.200	1.021	0.874	0.144	0.094
GCNT6	0.679	1.128	1.202	1.185	1.137	1.004	0.434	0.328

The concentration of MG remained unadsorbed in the dark (x) was calculated from the absorbance in table 3 using the linear equation of the calibration curve ($y = 0.0576x + 0.1241$). The concentration of unadsorbed MG was shown in table 4. Figure 6. Effect of contact time on the removal of MG, GCNT samples showed the same trend for all samples, that in the first 10 minutes very quick removal of MG occurred. Sample 3 and 2 showed the best removal where the remaining MG concentration was only 6.47 and 6.94 mg/l. After the first 10 minutes, a gradual desorption occurred and continued until contact time of 40 minutes, this may be attributed to the change in PH as a result of adsorption and releasing of hydrogen protons H^+, then the amount of the adsorbed MG on GCNTs started to increase gradually until the contact time reached 80 minutes. GCNT1 and GCNT5 samples showed the best adsorption where only 0.24 and 0.52 mg/l remained in the solution. Table 4 showed the results.

Table 4: Concentration of MG in mg/l remained unadsorbed in the dark on GCNTs

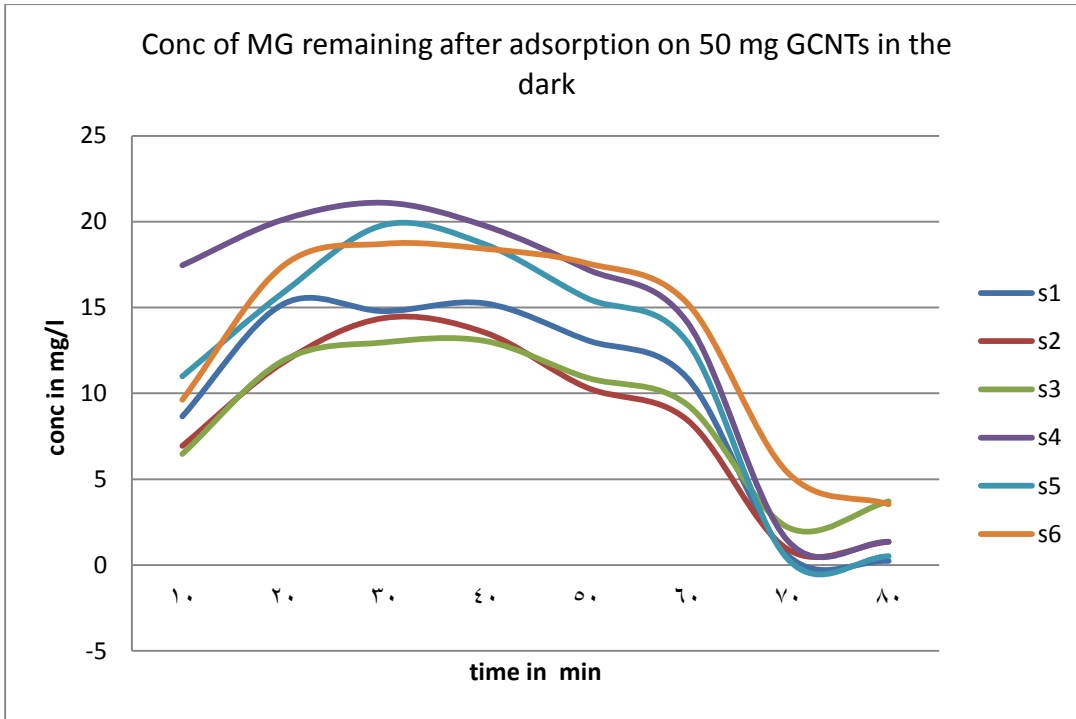| GCNT	10min	20 min	30 min	40 min	50 min	60 min	70 min	80 min
GCNT1	8.66	15.20	14.79	15.24	13.12	10.92	0.57	0.24
GCNT2	6.94	11.80	14.39	13.54	10.36	8.47	0.92	1.36
GCNT3	6.47	11.91	12.97	13.05	10.93	9.36	2.20	3.71
GCNT4	17.46	20.12	21.1	19.76	17.26	14.18	1.42	1.36
GCNT5	10.99	15.87	19.81	18.68	15.57	13.02	0.35	0.52
GCNT6	9.63	17.43	18.71	18.42	17.59	15.28	5.38	3.54

Fig. 6: Effect of contact time on the removal of MG = 250 mg /L; adsorbent dose =50 mg/50 ml; temp = 25 °C in the dark.

The adsorption efficiency of the six GCNTs samples at PH 9 and different contact times was calculated from the following equation;

$$q_t = V(C_0 - C_t)/m$$

Where q_t, represents the adsorption efficiency at time (t), V represents the volume of the MG solution in liters, C_0 and C_t are the concentration of MG at time zero t_0 and time t, m is the mass of the GCNTs in grams.

The GCNTs showed high adsorption efficiencies towards MG, all the GCNTs samples revealed efficiencies of more than 246 mg/g after 80 minutes. GCNT1 and GCNT5 showed the best adsorption efficiencies of 249.76 and 249.48 respectively. The results were shown in table 5 and figure 7. The adsorption efficiency of 384.62 mg/g, on graphene oxide was reported in the literature [20].

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Table 5: Adsorption efficiency of MG on GCNTs samples in mg/g in the dark

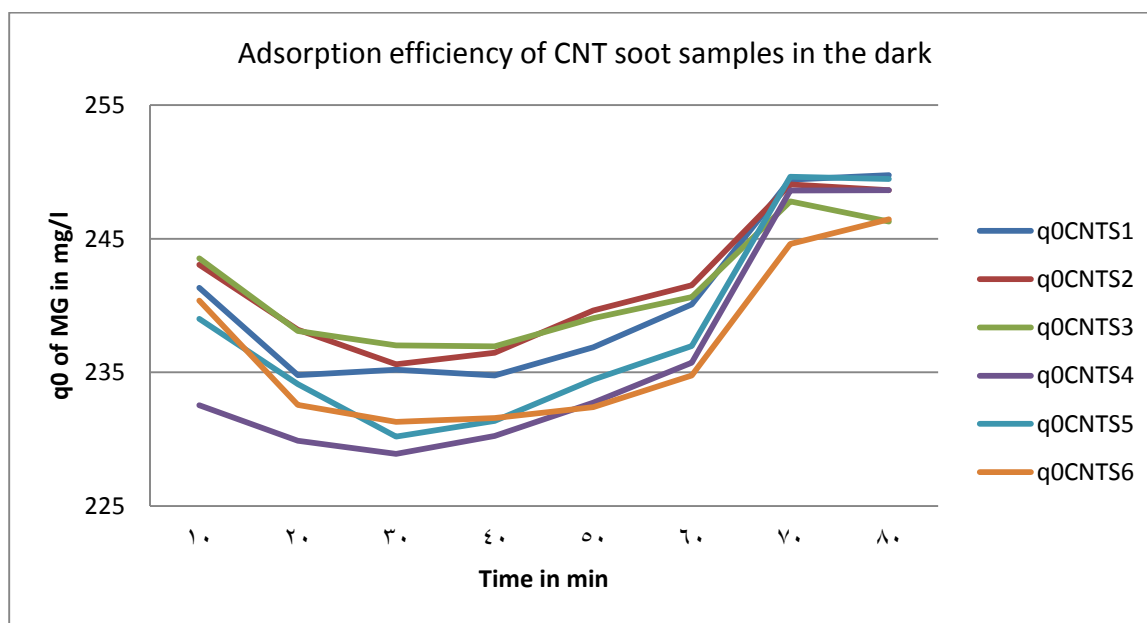| Time min	GCNT1	GCNT2	GCNT3	GCNT4	GCNT5	GCNT6
10	241.34	243.06	243.53	232.54	239.01	240.37
20	234.80	238.20	238.09	229.88	234.13	232.57
30	235.21	235.61	237.03	228.90	230.19	231.29
40	234.76	236.46	236.95	230.24	231.38	231.58
50	236.88	239.64	239.07	232.74	234.46	232.41
60	240.08	241.53	240.64	235.72	236.98	234.78
70	249.43	249.08	247.80	248.62	249.65	244.62
80	249.76	248.64	246.29	248.64	249.48	246.46

Fig. 7 : Adsorption efficiency of CNT soot samples in the dark

4.4. Adsorption of Malachite Green on GCNTs in the visible light

The calibration curve of malachite green (MG) used to calculate the adsorption efficiency read at 616 nm wavelength showed straight line with a linear equation of y= 0.0978 x + 0.0454 and a good correlation factor, R^2 = 0.9981. The concentration of the unadsorbed MG was calculated from the value of (x) at different absorbencies. The results were shown in table 6 and figure 8.

Table 6: Calibration curve of MG for the adsorption in the light:

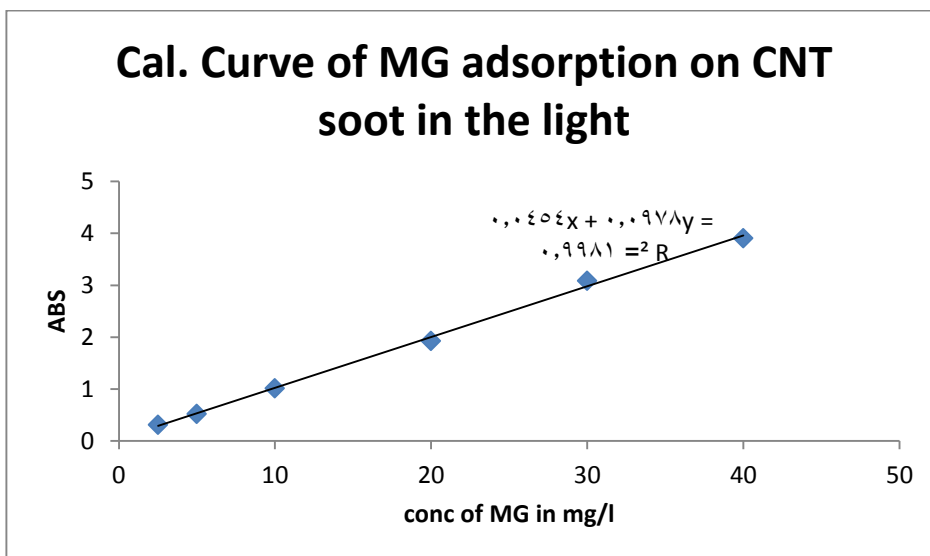| STD No.	STD Conc. in mg/l	Absorbance
1	2.5	0.314
2	5	0.522
3	10	1.018
4	20	1.929
5	30	3.090
6	40	3.91

Fig. 8: Calibration curve of MG for the visible light experiment.

The absorbance of the unadsorbed Mg and the remaining concentration in mg/l were shown in table 7 and 9 respectively. Fig. 9 showed the trend of amount of unadsorbed MG with time. The MG

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content in the solution decreased with increasing contact time, until reached the minimum at 130 minutes and then desorption process started and all curves began to ascend as seen in figure9. The concentrations of the MG (x) were calculated from the linear calibration curve equation $y = 0.0978x + 0.0454$.

Table 7: Absorbance of MG adsorbed on 50 mg GCNTs (50 ml of 250 mg/l MG) in the light:

Sample No.	10 min	30 min	50 min	70 min	90 min	110 min	130 min	150 min
GCNT1	4.42	3.37	1.45	0.89	0.302	0.266	0.165	0.208
GCNT2	4.17	3.25	1.00	0.76	0.437	0.451	0.272	0.352
GCNT3	4.37	3.49	1.39	1.230	0.838	0.759	0.532	0.670
GCNT4	5.77	4.68	2.01	1.200	0.726	0.576	0.323	0.445
GCNT5	4.43	3.43	1.53	1.06	0.610	0.448	0.218	0.331
GCNT6	4.63	3.49	2.00	1.3	0.765	0.503	0.279	0.321

Table 8: Concentration of MG remained unadsorbed in the light on 50 mg GCNT .

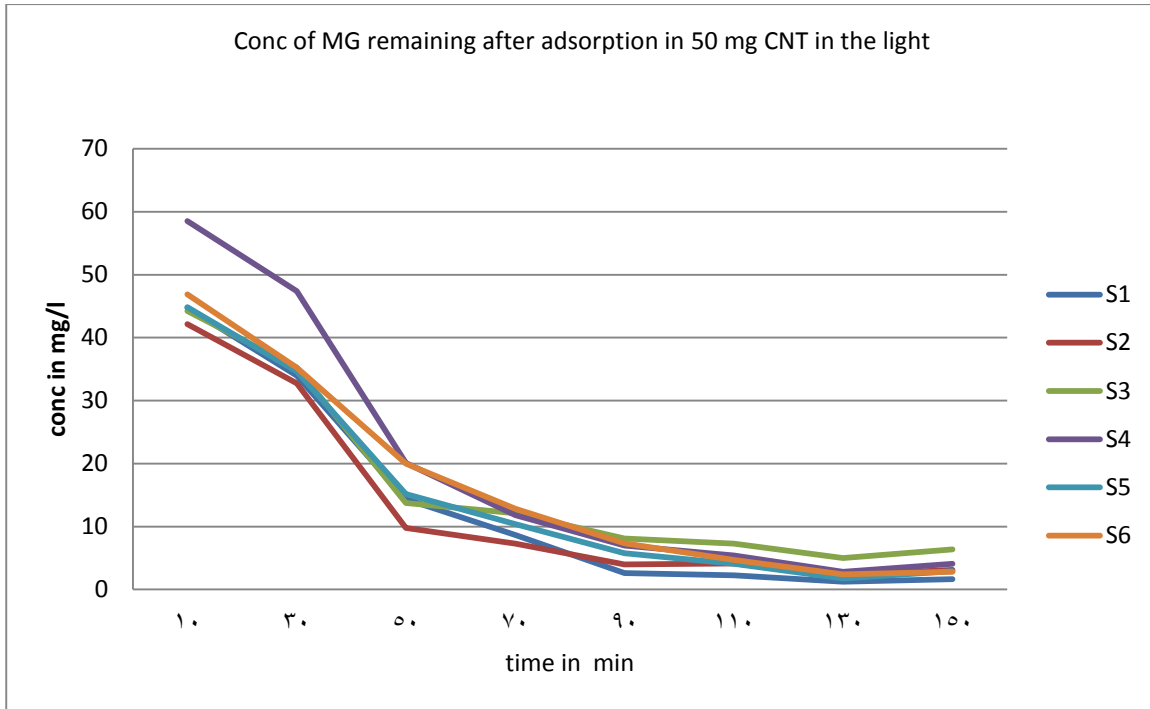| sample No.	10 min	30 min	50 min	70 min	90 min	110 min	130 min	150 min
GCNT1	44.73	33.99	14.36	8.64	2.62	2.26	1.22	1.66
GCNT2	42.17	32.77	9.76	7.31	4.00	4.15	2.32	3.13
GCNT3	44.22	35.22	13.75	12.11	8.10	7.30	4.98	6.39
GCNT4	58.53	47.39	20.09	11.81	6.96	5.43	2.84	4.09
GCNT5	44.83	34.61	15.18	10.37	5.77	4.11	1.77	2.92
GCNT6	46.88	35.22	19.99	12.83	7.36	4.68	2.39	2.82

Fig. 9: Trend curve of MG unadsorbed in the light.

The adsorption efficiency of the six samples was calculated from the former used equation;

$$q_t = V(C_0 - C_t)/m$$

The adsorption efficiency increased with increasing contact time until the GCNTs reached the saturation at 130 minute . At this period , GCNT1 showed the best removal capacity (248.78 mg/g), while GCNT3 showed the least efficiency (245.02 mg/g) , then all the efficiencies start to decrease indicating a desorption process. Table 9 and figure 10 showed the results.

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Table 9: The adsorption efficiency of GCNTs towards MG in the light

| Time in min	q_t GCNT1	q_t GCNT2	q_t GCNT3	q_t GCNT4	q_t GCNT5	q_t GCNT6
10	205.27	207.83	205.78	191.47	204.17	203.18
30	216.1	217.23	214.78	202.61	215.39	214.78
50	235.64	240.24	236.25	229.91	235.82	230.01
70	241.36	242.69	237.89	238.19	239.63	237.17
90	247.38	246.00	241.9	243.04	244.23	242.64
110	247.74	245.85	242.70	244.57	245.80	245.32
130	248.78	247.68	245.02	247.16	248.23	247.61
150	248.34	246.87	243.69	245.91	247.18	247.18
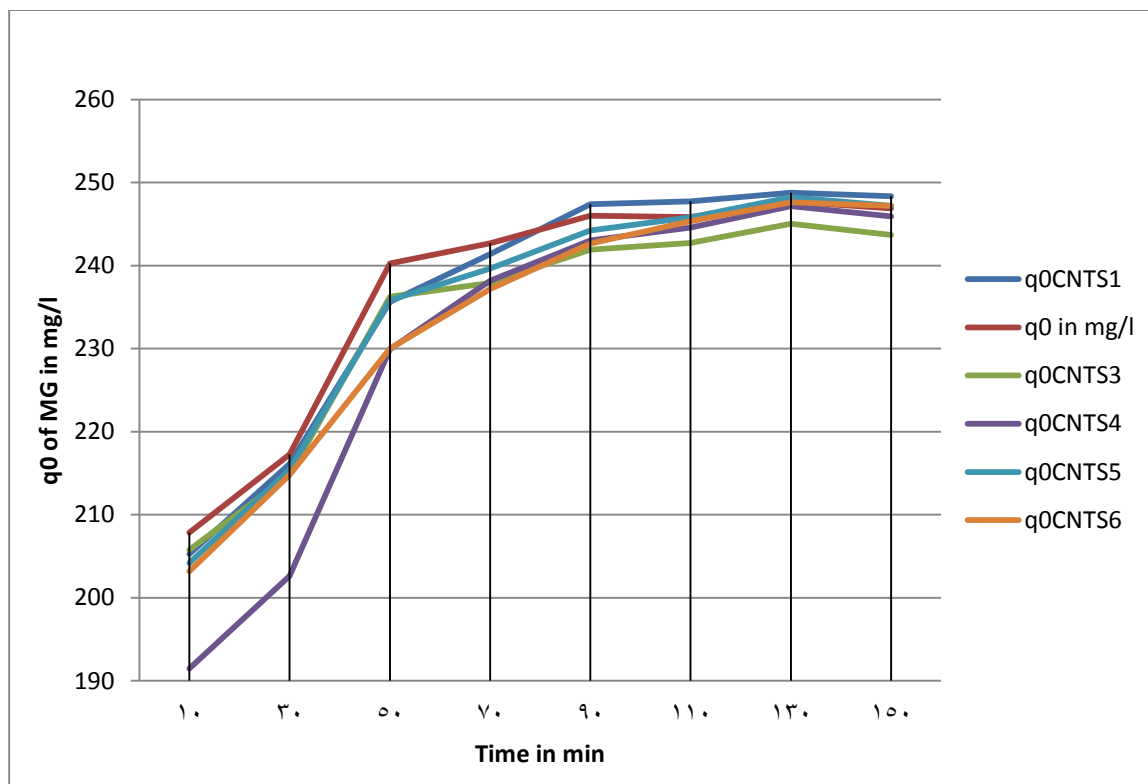
Fig. 10: Adsorption efficiency of the six GCNTs samples in the light

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6. Conclusion

Six Graphitic Carbon Nanotubes (GCNTs) were prepared on commercial stainless steel cylinder by catalytic chemical vapor deposition method using ethyl alcohol as a carbon source. The samples were purified and characterized by EDX, SEM and TEM which confirmed the presence of GCNTs. The graphitic carbon nanotubes were used as adsorbents to remove the organic pollutant malachite green dye from synthetic water sample in the dark and visible light. The six GCNTs showed removal efficiency of 249.43, 249.08, 247.80, 248.62, 249.65 and 244.62 mg/g respectively for the dye in the dark at 70 minutes contact time. The equilibrium time for the maximum removal efficiency in the visible light was longer (130 minutes) and the removal efficiencies are 248.78, 247.68, 245.02, 247.16, 248.23 and 247.61 mg/g respectively.

5. Recommendations

The researcher recommends further studies on the synthesis of carbon nanotubes on stainless steel. Researches on adsorption capacity of graphitic CNT and other applications such as optical properties and composite materials are also recommended. Removal of organic pollutants from water and waste water by graphitic carbon nanotubes is a recent topic of scientific researches.

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