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A Review: Carbon Nanotubes Toxicity Effects on The Respiratory System and Skin

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ABSTRACT

Nowadays, Carbon nanotubes have been widely used in industry, engineering, science, and many other fields. The CNTs are formed of two classes, the first class is single-wall (SWCNTs) and the second is multi-wall (MWCNTs). Their synthesis is implemented using various methods such as Arc discharge and chemical vapor deposition processes. These methods produce stripping carbon atoms which exist as carbon whiskers formed as a side product in the air that could be breathed by human in the factories. These broad applications directly affect the human health because they are related to important areas involving direct influence to human health for example, in the pharmaceutical and food industries. One of the main risks facing the use of carbon nanotubes is to study the toxicity and the possibility of causing serious diseases such as lung cancer and skin cancer. As mentioned in the results of published researches explored in this review, especially those related to studying the effect of carbon nanotube on rat groups, for instance, direct exposure to specific amounts of carbon nanoparticles has caused serious complications, fibrosis and the emergence of carcinogenic infections in lung cells. Studies have shown that the toxicity of carbon nanotubes exceeded the toxicity of known toxic compounds such as quartz. These results, which have been discussed in the research, indicate that nanoparticles are considered as a toxic substance and we should be very cautious when dealing with them and take the necessary precautions in the laboratory especially those related to human health and food industries.

1. INTRODUCTION

Nanotechnology has been the most interesting branch in scientific field which deals with Nano-scale matter as Nano particles it can be defined as very small particles in size that have special physical and chemical features like Nano regulated size (1-100 nm)[1]. The ratio of surface area to mass is great, excellent reactivity and also functional construction[2].

The Nanostructures also has exception physical and chemical features, elucidating high solubility and reactivity in addition to improved stability more than the original compound. The development compound, which is produced by Nanotechnology, has reworking possibility on conventional materials in view of better efficiency.

In other words, Nanotechnology can be defined according to National Science Foundation and NNI, as the capability of understanding and controlling of matter manipulation at the individual atoms and molecules level. The carbon nanotubes (CNTs) have

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exceptional physical, chemical and electronic features that make them more interest in several important medical applications[2, 3] although most researches have evaluated the pharmacological activity and toxicity of CNTs[1, 4]. The toxic effects of carbon nanotube will be evaluated by comprehensive analysis of human health in the present investigation.

2. CARBON NANOTUBES TYPES

The Carbon Nanotubes (CNT) can be classified into various types depending on its topologies and shapes:

2.1. Single-Walled Nanotubes The first type of carbon Nanotubes is a Single-Walled Nanotubes (SWNT) has a one nm of closed diameter, and many million times longer of length. The structure of a SWNT is called graphene, which is formed by wrapping layer with one atom thick of graphite into a seamless cylinder of CNT. Graphene sheet is a wrapped way which exhibited by indices pair (n, m) called the chiral vector, which is the unit of vector number to both directions in the graphene honeycomb crystal lattice[5]. When m value equal to 0, the Nanotubes appeared as "zigzag" called for the hexagons pattern as moving in tube circumference. Meanwhile if n is equal to m , the nanotubes become armchair, (fig. 1) explained one type of cyclohexene. A hexagon of carbon atoms, on the other hands, is known "chiral", if m value is between zigzag and armchair structures.[6, 7]

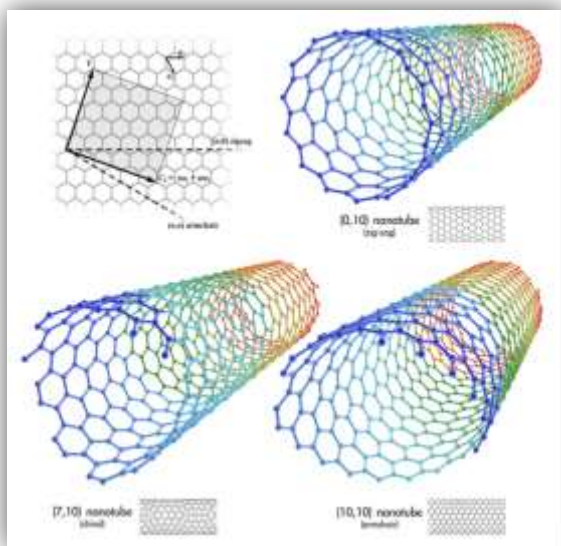


Fig .1: Single-Walled Nanotubes (SWNT) Cyclohexene a hexagon of SWCNT carbon atoms [8, 9]

2.2. Multiple Walled Carbon Nanotubes (MWCNTs)

MWCNTs consist of many coaxial cylinders that is constructed from single grapheme sheet encirclement a hollow core. The outer diameter of MWNTs was (2-100) nm, and inner diameter was (1-3) nm, with one to several mm lengths. There are two classifications of MWCNTs structures according to their graphite layers arrangements : the first consists of a parchment-like structure formed graphene sheet warping around it while the other classification is called Russian doll model that has multilayer of graphene sheets which are arranged in a concentric structure (figure2)[9, 10].

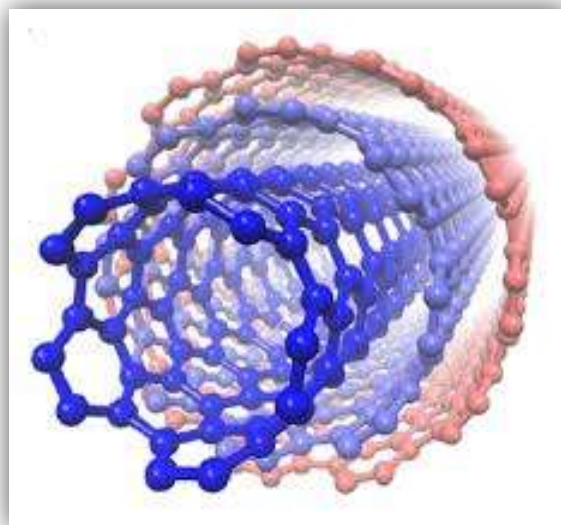


Fig .2: Multiple walled carbon nanotubes [9]

3. CARBON NANOTUBE SYNTHESIS METHODS

Many uses of Carbon Nanotube like composite materials that need big quantities of nanotubes and industrial-scale synthesis methods which lead to economically feasible, require an economic method for large-scale CNT production. Many CNT production methods can be used for SWCNT and MWCNTs synthesis.

3.1. Arc Discharge Method

The production of high quality nanotubes is implemented by the arc-evaporation method by using about fifty amps of current between double graphite electrodes in helium atmosphere, which causes graphite evaporation. Several were condensing on the wall of reaction vessel, while others on the cathode that included the nanotubes of carbon. When Co and

Ni or other metal is added to the anode, a single-walled nanotubes are made. The tubes formed by this method are similar to that used for the fullerene maker[11]. Other structure is formed in the carbon electrode negative end has 4 - 30 nm of diameter in addition to length up to 1 mm, it uses carbon evaporation in an argon-filled vessel (100 Torr) for the direct current (dc) arc-discharge . The quality of carbon nanotubes, which is made by this way, is poorer than those in arc-evaporation, but this method is developed in recent years. Fig (3) shows two configurations of arc-discharge method to produce SWCNT with aid of catalyst and MWCNT without the catalyst[12,13].

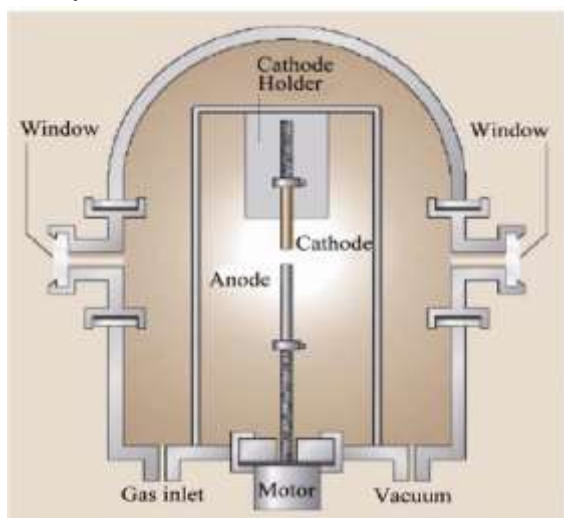


Fig.3: Arc-discharge method to produce SWCNT with aid of catalyst and MWCNT without the catalyst[12]

3.2. Chemical Vapor Deposition (CVD)

Although large quantities of un purified nanotubes produced by arc discharge, several improvements were enrolled in production and controlling of nanotubes synthesis. The chemical vapor deposition (CVD) is a process which introduces a good choice to get a manageable process for nanotubes synthesis with predefined properties. The chemical vapour deposition is a process which feed stocks of hydrocarbon or carbon monoxide catalytic decomposition in addition to supported transition metal catalysts. It is implemented in two steps[14, 15]:

a) The Metal catalysts Ni, Fe or Co. then the core of

catalyst is loaded by thermal annealing or chemical etching. Ammonia is used as an etchant.

b) Then Carbon source is placed in gas phase in the chamber of reaction. After this plasma or heated coil is used for converted carbon molecule to atomic level.

c) Diffusion is towards substrate and conversion by catalyst; the Nanotubes are formed outer the metal catalyst. Methane, carbon monoxide or acetylene are sources of carbon. Finally the temperature degree is used for nanotubes maker ranged 650 – 9000 °C while the typical yield is 30.

By this method, many carbon Nanotubes structures are made like amorphous carbon layers on the catalyst surface, amorphous carbon filaments, metal particles are covered by graphite layers, the SWNTs and MWNTs synthesized by well-crystallized graphite layers. The nanotubes growth mechanism in the Chemical Vapor Deposition process use the hydrocarbon molecules catalyzed dissociation in the present of transition metal, in addition to carbon atoms saturation in the metal nanoparticle. The precipitation of carbon from the metal particle is resulted in production tubular carbon solids in the sp² [5, 11]. The features of the carbon Nanotubes are synthesized by CVD method based on the conditions of the work like temperature , pressure of operation, concentration and volume of hydrocarbon, also nature and kind, metallic catalyst size and pre-treatment, support architecture and reaction period (Fig 4).

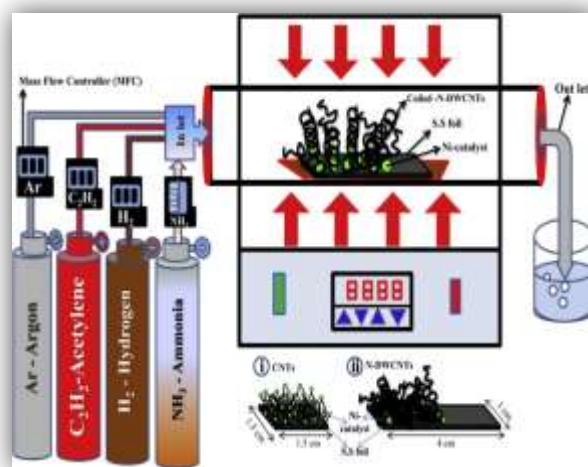


Fig.4:CVD method to produce MWCNT[15].

4. CARBON NANOTUBE APPLICATIONS

Various applications of CNTs were developed and invented in recent years as below[16, 17]:

4.1. The carrier of Drug Delivery: the Carbon nanohorns (CNHs) are characterized as circular gathering with irregular horn. Investigation proved that CNTs and CNHs are a possibility carrier to drug delivery system.

4.2. Biotechnology Applications: In genetic engineering which is more important field in biotechnology, CNTs and CNHs are used to gene transfer while the atoms are useful for bio imaging genomes development, proteomics and tissue engineering. The single stranded of DNA warped around SWNT by linked with specific nucleotides led to change in its electrostatic property.

4.3. Artificial Implants: The nanotubes and nanohorns can be used for avoiding implants rejection in the body by attachment with different proteins. In addition of application in artificial joints to avoid host rejection reaction and as a results of carbon nanotubes.

4.4. High Tensile Strength, it is filled with calcium and grouped in the structure of bone which can be acted as bone substitute.

4.5. CNT usage As Catalyst

The use of CNT imply a big surface area and hence, the molecular catalyst level leads to release nanotube in suitable rate at desired time. Thus, the decrease of catalyst in addition to frequency and amount can be implemented using CNTs.

4.6. Biosensors Applications

CNTs act as sensing materials for different conditions including pressure, thermal, flow, gas, mass, optical, position, strain, biological sensors and stress chemical. It causes huge changes in different field of Biomedical. Glucose sensing application is an example of it. Also hazardous radiation exposure is measured by biosensors like CNT biosensors are used in nuclear plants, chemical laboratories, industries and other applications (Figure 5).



Fig.5: Various CNT applications in industry and Biotechnology[16].

5. CARBON NANOTUBES TOXICITY

The potential medical applications of carbon nanotubes (CNTs) are resulted from exceptional physical, chemical and electronic features. Several investigations have studied the Carbon nanotubes pharmacological efficacy, toxicity and stability. In SWNTs and MWNTs applications researchers suspected toxicity because of the non-biodegradable structure and its resemblance to needle-like, carcinogenic asbestos fibers in its shape, size and cellular persistence.

5.1. Effects of MWCNT on Human Health

The MWCNTs produced by burning fuel-gas are present indoor and outdoor[4] consist of airborne particulate collection has size lower than 2.5 μm . Different sources of MWCNT such as the combustion of fuel from plants power, burning wood, also industrial ways and buses and trucks fuel like diesel-powered. Immune response was influenced by the length and shape of the CNTs that specify the transfer mechanism through macrophage cell membrane[18]. Less CNTs ($\sim 0.22 \mu\text{m}$ in length) can transfer through membrane than the longer (0.8 μm) CNTs which improved the use in animal experimental model that

found the shorter CNTs were inserted into subcutaneous tissue whereas the longer CNTs causing inflammation. The conflict source can be produced from the diversity between defect and densities of charge for several types of CNTs. then it may be wise to segregate CNTs with similar charge densities and lengths.

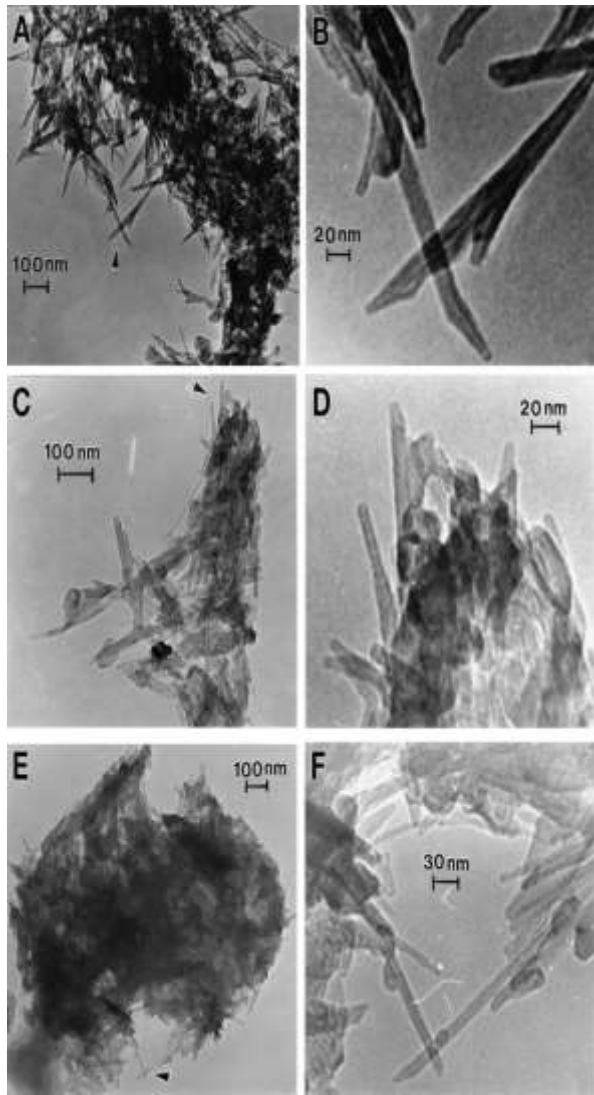


Fig.6: Natural Gas SEM. (A) a transmission electron microscope (TEM) a particulate matter (PM) sample. (B) High magnification of the area marked by the arrow in (A). (C) TEM snap of an environmental PM sample. (D) High magnification of the area marked by the arrow in (C). (E) TEM snap of an outdoor PM sample (F) High magnification of the area marked by the arrow in (E)[19].

5.2. Effects of SWCNT on Human Natural Health

The effects of SWCNT on human health were studied by many researchers. They found that the inhalation of SWCNT causes severe inflammatory response and fibrosis. Pneumoconiosis was recorded in worker Exposure to carbonaceous materials for both natural and manmade graphite. Also severe symptomatic patients with massive pulmonary fibrosis appeared through carbon electrode production. Several infections were observed in the upper respiratory tract included, pneumonia incidence in 746 graphite workers in addition to chronic bronchitis. Hypertrophic laryngitis, giofibroma , papillomatous bronchitis of the larynx, may be precancerous lesions as investigations recorded[20].

The exposure to manufacturing conditions may cause different infections. In the current study, the outcomes of exposure to aerosolize respire able SWCNT causes lung burden in animal lab. This lung burden was observed in workers exposed to the peak airborne concentrations for one year which were measured in an occupational setting .Investigations results are considered important for assessment of the permissible exposure level (PEL) for SWCNT which PEL detected by Occupational Safety and Health Administration for respire-able graphite dust. According to an output of inhalation studies, one can conclude that if cases were long-period exposures to SWCNT at current PEL for synthetic graphite, the risk of pulmonary changes may be happened[21].

5.3. Effects of SWCNT on Human Skin-Cells

Many studies deal with the effect of SWCNTs on the skin cells in vitro. The human epidermal keratinocytes (HEKs) cells were studied for this purpose. It was treated with raw HiPco CNTs (consist of iron 30%, and similar to the raw HiPco product at 0.06, 0.12, or 0.24 mg/ml for 18 h) which let to free radicals formation in the cells treated with SWCNTs, In the aggregation of peroxidative products, total sulfhydryl's decreased with amount of vitamin E reduction. Oxidative stress in these results caused by carbon nanotubes because several iron materials activated oxidation or peroxidation in cells[20, 22].

5.4 .Effects of MWCNT on Human Skin-Cells

The Effects of MWCNT on Human Skin-Cells was also investigated. The MWCNTs can enter human keratinocytes by different mechanism which has been elucidated. This did not provide information about how structures were a risk to be exposed to persons since keratinocyte cultures missed the protective stratum barrier seen with intact skin. MWCNT can localize intracellular and cause keratinocytes irritation. The Exposure should be assessment before the detection of hazard risk in environmental field. The effect of multi-walled carbon nanotubes in keratinocyte viability and IL-8 release shown in fig.7 [23].

6. MECHANISMS OF CNT ATTACK ON HUMAN BIOLOGICAL CELLS

The immune response and penetrating the macrophage cell membrane are affected by the length and shape of the CNTs[19]. They were best inserted in a macrophages and phagocytes cells than bigger length (0.8 μm). Phagocytosis is a process that penetrates materials inside cells it the same as the endocytosis, but it swallows bigger particles, like bacteria ($\sim 1 \mu\text{m}$). Many researches implicate endocytosis/phagocytosis as the cellular swallow pathway of CNTs as in Figure (7).

The Nano penetration is a passive process of how nanomaterial's transfer across cellular membrane without energy dependent as in figure (8). In this process, passive diffusion of nano-needles bring inside the cell, The CNTs may behave as cell penetrating peptides (CPPs), this finds sequences of poly-cationic that encourage proteins to uptake into mammalian cells. These studies pointed that f-CNTs are similar to CPPs in structure and they have total charge which may more likely penetrate the plasma membrane.

The mechanism of CNTs toxicity to the cell are more interesting. Investigations pointed that CNTs may induce harmful effect on cells by several pathway inductions like DNA damage. In a research, mesothelial cells treated with SWCNTs ($\sim 25 \mu\text{g}/\text{cm}^2$) cause generated DNA recovery with changes in the cell cycle which lead to trigger apoptotic signals. It is also observed that the interaction between CNT/DNA in a three hour incubation with $96 \mu\text{g}$ SWCNT/ cm^2 generated DNA degradation in

lung fibroblasts, the observation of specific toxic observation result from the treatment with other f-

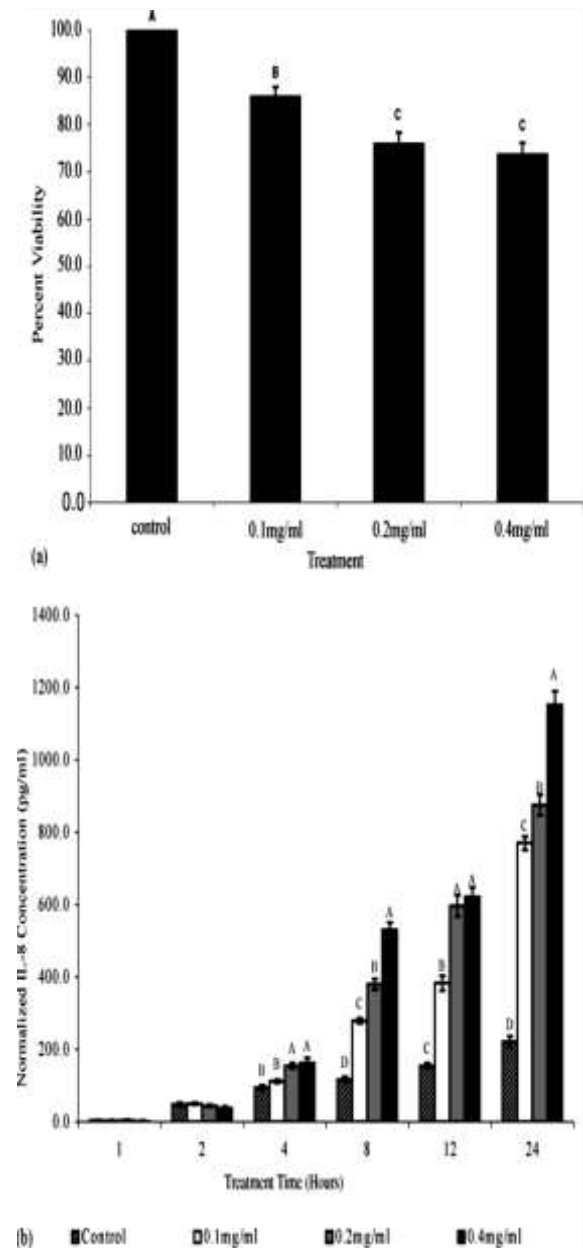


Fig.7: The effect of multi-walled carbon nanotubes in keratinocyte viability and IL-8 release. (a) Mean viability of the HEKs 24 h following exposure to MWCNT. (b) IL-8 increases with time and concentration of MWCNT. Different letters (A, B, and C) pointed to statistically significant at $P < 0.05$ [23].

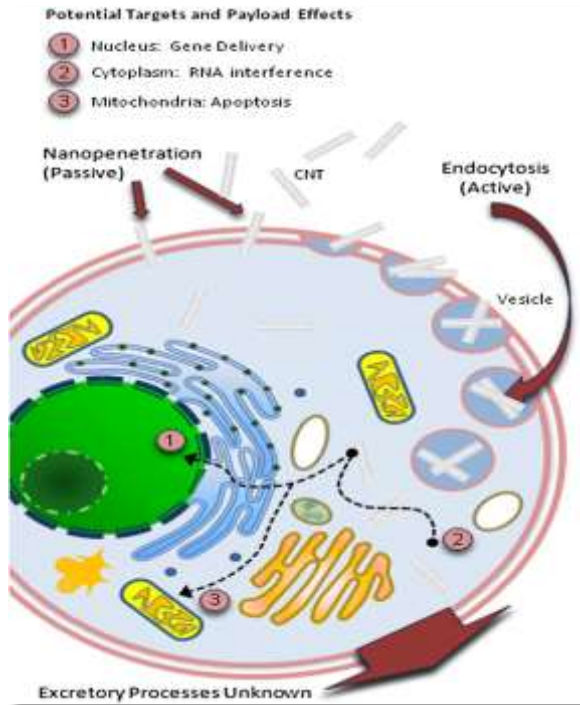


Fig.8: Receptor-mediated endocytosis or nanopenetration, which is functionalization dependent, are suggested as possible mechanisms for CNT interactions with cells. Although preliminary studies have probed targeting capability of CNTs vis-à-vis distinct organelles[18]

7. CONCLUSIONS

From the above discussion, we have observed that CNTs are regarded as a high toxic material with all its forms. Comparative studies on the nanoparticles effect on human health have shown that there are real risks to health because nanoparticles have physical properties that make them toxic, such as high surface area and fine fibrous shape. Experiments in animal's laboratory showed that carbon nanoparticles were able to induce inflammation, fibrosis, epithelial granuloma, and biochemical toxicity causes alteration in the lungs, which impaired the function of lung. The studies of inhalation toxicity are important to clarify whether CNT molecules interact to the lung causing lesions. The results of inhalation exposure investigations allow evaluation the effects of CNTs in upper respiratory tract and measured exposure limit. The limit of occupational and risk exposure, CNTs cannot be treated as normal industrial product.

The SWCNT studies show the effects of SWCNT on human epidermal keratinocytes to generate oxidative stress and cause cellular toxicity by free radicals production, peroxidative products accumulation, antioxidant declined, and cell viability losing after 18h. Also it causes changes in ultra-structural and morphological of human cells in vivo. Data suggested that unrefined SWCNT exposure can lead to quickened oxidative stress and generated dermal toxicity in exposed workers.

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الآثار السمية لأنابيب الكربون النانوية على الجهاز التنفسي والجلد

أستبرق وفيق غياض و يسرى محمود العبيدي

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الخلاصة:

في الوقت الحاضر، تم استخدام الأنابيب النانوية الكربونية على نطاق واسع في الصناعة والهندسة والعلوم والعديد من المجالات الأخرى. تتكون الأنابيب النانوية الكربونية من نوعين، النوع الأول هو الأنابيب النانوية أحادية الجدران (SWCNTs) والثاني الأنابيب النانوية متعددة الجدران (MWCNTs). يتم تحضير أنابيب الكربون النانوية باستخدام طرق مختلفة مثل عمليات تفريغ القوس وترسيب البخار الكيميائي. تنتج هذه الطرق ذرات الكربون على شكل شعيرات الكربون التي تتشكل كنتاج ثانوي في الهواء يمكن أن يتنفسه الإنسان في المصانع. تؤثر هذه التطبيقات الواسعة بشكل مباشر على صحة الإنسان لأنها ترتبط بمجالات مهمة تنطوي على تأثير مباشر على صحة الإنسان، على سبيل المثال، في الصناعات الدوائية والغذائية. أحد المخاطر الرئيسية التي تواجه استخدام أنابيب الكربون النانوية هو دراسة السمية وإمكانية التسبب في أمراض خطيرة مثل سرطان الرئة وسرطان الجلد. كما ذكر في نتائج الأبحاث المنشورة التي تم عرضها في هذه المقالة، وخاصة تلك المتعلقة بدراسة تأثير الأنابيب النانوية الكربونية على مجموعات الفئران، على سبيل المثال، تسبب التعرض المباشر لكميات محددة من الجسيمات النانوية الكربونية في حدوث مضاعفات خطيرة وتليف وظهور التهابات مسرطنة في خلايا الرئة. وقد أظهرت الدراسات أن سمية الأنابيب النانوية الكربونية تجاوزت سمية المركبات السامة المعروفة مثل الكوارتز. تشير هذه النتائج، التي تمت مناقشتها في البحث، إلى أن الجسيمات النانوية تعتبر مادة سامة ويجب توخي الحذر الشديد عند التعامل معها واتخاذ الاحتياطات اللازمة في المختبر خاصة تلك المتعلقة بصحة الإنسان والصناعات الغذائية.