Management radioactive nuclear waste (Strontium Hydroxide) by carbon nanotubes prepared by laser ablation

معالجة المخلفات النووية المشعة (هايدروكسيد السترونتيوم) بواسطة أنابيب الكاربون النانوية التي المحضرة بطريقة الاقتلاع بالليزر

Thuraya A. Abdul Hussian **Ghufran. S. Jaber**

Radiography techniques department, Al-Turath University College

Abstract

In an attempt to find an appropriate method to management nuclear waste to prevent pollution in the environment as a result of leaching ion and thus threatens our environment and our health. In this research the nuclear waste (Strontium hydroxide) was management by immobilization nuclear waste by Carbon nanotubes (CNTs). Carbon nanotubes were produced in simple step by using laser ablation method. To prepare CNTs the Nd-YAG laser were bombing the graphite target in a deionized water was used. The next step adding $Sr(HO)_2$ powder to the CNTs solution with calculations ratio. To get homogenous mixing of CNTs-$Sr(OH)_2$ the solution was putting in the centrifuges. The strontium hydroxide absorbs carbon dioxide from the air to form strontium carbonate so, the new solution is CNTs-$SrCO_3$. To dry the new solution three drops was applied on the glass slides above heater with (60-80) C^o. To investigate the radiation damage on carbon nanotube structure, the sample was irradiation by Beta source ($^{90}Sr/^{90}Y$) for different period of time (1hour and 720 hour).

X-ray diffraction XRD was used to measure structure, properties, while scanning electron microscope SEM was used to measure shape and size. The results revealed a homogeneous distribution of nanoparticles with an average particle size of approximately 20nm. The XRD spectra for all samples before and after irradiation show higher peaks that almost appear at 2 θ = 25 degree. It's clear that increasing the radiation dose has little effect on the location of the peaks of all samples, implying that the phase of the material did not change.

From SEM micrograph, CNTs-$SrCO_3$ were well decorated the surface of CNTs and there was not any remarkable difference in the corresponding due to Beta radiation exposure.

***Keywords*:** waste management, Carbon Nanotubes (CNTs), laser ablation (PLAL), nuclear waste**,** Strontium hydroxide.

الخلاصة:

في محاولة لإيجاد طريقة مناسبة لإدارة المخلفات النووية لمنع تسرب الأيونات إلى المناطق المحيطة وتهدد بيئتنا وصحتنا. في هذا البحث ، تمت معالجة النفايات النووية (هيدروكسيد السترونتيوم) عن طريق تثبيت النفايات النووية بواسطة انابيب الكاربون النانوية (CNTs). تم تحضير انابيب الكاربون النانوية بخطوة بسيطة باستخدام طريقة الاقتلاع بالليزر.

لتحضير انابيب الكاربون النانوية ، تم استخدام ليزر Nd-YAG بطول موجة 1064 نانومتر ، وبطاقة 750 مللي جول و 100 نبضة لقصف هدف الجرافيت الموضوع داخل ماء منزوع الأيونات. الخطوة التالية اضافة مسحوق $Sr\ (HO)_2$ إلى محلول CNTs بنسب محسوبة. للحصول على خلط متجانس من $CNTs\text{-}Sr\ (OH)_2$، ثم وضع المحلول في جهاز الطرد المركزي. ان محلول هيدروكسيد السترونتيوم يمتص ثاني أوكسيد الكاربون من الهواء لتكوين كربونات السترونتيوم ، لذا فإن المحلول الجديد هو $CNTs\text{-}SrCO_3$. لتجفيف المحلول الجديد ، تم وضع ثلاث قطرات على شرائح زجاجية فوق سخان بحرارة (60-80) درجة مئوية. و للتحقق من الضرر الإشعاعي على بنية انابيب الكاربون النانوية ، تم تشعيع العينة بمصدر بيتا (Sr / $^{90}Y^{90}$) لفترات زمنية مختلفة (1 ساعة و 720 ساعة).

استخدم حيود الأشعة السينية XRD لقياس البنية والخصائص ، بينما تم استخدام المجهر الإلكتروني الماسح الضوئي SEM لقياس الشكل والحجم. كشفت النتائج عن توزيع متجانس للجسيمات النانوية بمتوسط حجم الجسيمات النانوية بما يقارب 20 نانومتر. تُظهر أطياف XRD لجميع العينات قبل وبعد التشعيع وجوود قممً تظهر تقريبًا عند $2\theta = 25$ درجة. ومن الواضح أن زيادة الجرع الإشعاعية لها تأثير ضئيل على موقع قمم جميع العينات ، ما يعني أن تركيب المادة لم تتغير.

و من الصور المجهرية SEM ,تزيين CNTs-SrCO3 سطح انابيب الكاربون النانوية بشكل جيد جيدًا ولم يكن هناك أي اختلاف ملحوظ في المقابل نتيجة التعرض لإشعاع بيتا.

1-Introduction:

Nanomaterial's have received widespread scientific, technical, and medical interest in recent years due to their miraculous properties as opposed to larger-sized materials. Furthermore, nanomaterial's are used in a variety of applications that save people's lives. As well as the manufacture of nuclear fuels, structural components, separation processes, and waste treatment [1].

Carbon nanotubes (CNTs), have wonderful properties that help it to use frequently for nuclear waste management. CNTs were formed from graphitic carbon material where, used for nuclear waste storage due to their attractive structural and physicochemical property in the nano-range of large ability CNTs form a hollow cylinder usually closed at one end, with the length-to-diameter ratio of $\leq 10^6$ [2]. There are two types of CNTs structure either single-walled (SW) or multiwall (MW), as shown in the Transmission electron microscopy figure 1 (a, b and c), respectively. Each wall of the structure of a flat molecular network of carbon atoms known as graphene, but graphite is the material consisting of graphene panels overlapped. Parties covers carbon nanotubes include five-rings to suit bending geodesic. The distance between the walls in MWNTs are within a few A [3]

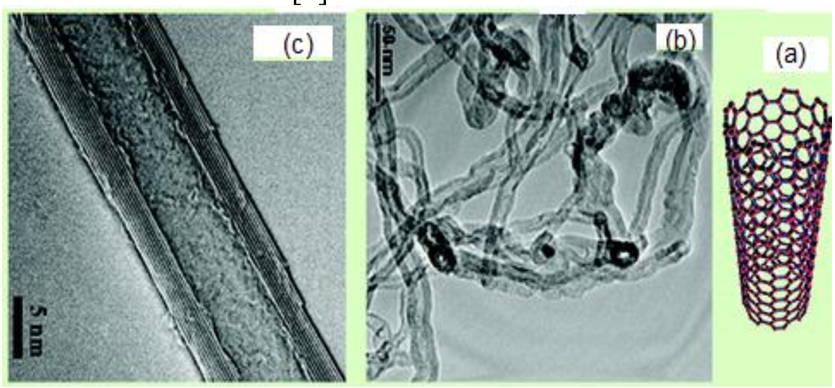


Fig (1): (a) SEM image of the CNT structure (b) Transmission electron microscopy pattern of a bundle of CNT in fabricated by CVD route and (c) High resolution microscope for MWNT [4].

There are several methods to produce CNTs, like arc discharge, laser ablation and chemical vapor deposition (CVD). This type of materiel exists in physical forms: as a powder or bucky-paper. CNTs have been used at the laboratory scale to adsorb several trace contaminants from water [5], and have also been suggested as a super absorbent for dioxin removal. None the less, there is still a lacking accommodating of the basic physics and chemistry of the interaction between a CNT surface and adsorbed species [6].

At this research, we briefly study the ability of using CNTs to immobilize nuclear waste (Strontium hydroxide) to stop leaching ions to the environment which causing nuclear waste pollution that effecting on the human being and environment [7].

Strontium is a soft, silver-yellow caller and alkaline-earth metal. It has three crystalline forms and some of its physical and chemical properties is similar to calcium and barium. ^{90}Sr has a half-life of 29.1 years. ^{90}Sr used industrially to measure the thickness of paper, plastic, rubber and metal foils. In medical applications ^{90}Sr used for treatment of some eye and skin cancer. One of the most important applications of ^{90}Sr it is an isotopic energy source used in various research applications, such as radioisotope thermoelectric generators (RTG) [8].

Radioactive form of strontium is much more health risk than stable strontium. The radioactive ^{90} Sr are longer-lived fission products produced.^{90}Sr is unstable decay by emitting Beta particle to convert ^{90}Sr to stable zirconium [9].

2-Experimantal work:

CNTs has been prepared by using Nd:Yag laser with wave length1064 nm at frequency 1Hz (pulsed laser ablation in liquid) as shown in figure 2.

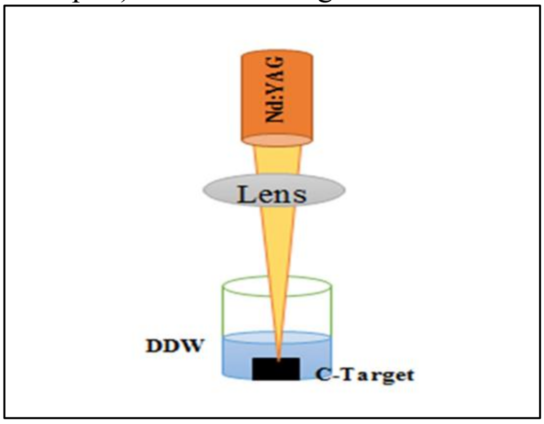


Fig (2): Schematic diagram of CNT-NPs prepared by laser ablation in liquid.

The Nd-YAG laser-ray is focusing by a lens on a C-target. The C-target was putted at glass container. Then immersed in 1ml of di-ionized water (DDW) all process at room temperature. The Nd:Yag laser energy (750 mJ and no. of pulses=100) the distance between lens and target =4 cm. After preparation CNT-NPs, dilute 0.43 g of $Sr(OH)_2$ in 1 ml of carbon nanotubes was prepared by laser then use the centrifuge for 2 minutes to get homogenous mixture. After that, 3dropes was taken from the homogenous mixture these drops were dropped one by one, on a plate of glass above heater on temperature (60-80) C^o to dry the samples. CNT-NPs prepared at University of Technology, at laser lab.

To simulate effect of radiation on the carbon nanotubes structure, the samples were irradiated by Beta particles emitted from radioisotope ^{90}Sr/^{90}Y source. ^{90}Sr/^{90}Y emitting Beta with activity 0.6 Ci and absorbed dose $6 \times 10^4 Gy/hr$. The samples were placed at 15 cm from the source for a different period of time as shown in the Table 1.

Table (1): The time of exposure to gamma rays and the doses of irradiation Beta particle.

Dose rate	Time of exposure samples of Beta radiation
$6 \times 10^4 Gy/hr$	1 hr
$4320 \times 10^4 Gy/hr$	720 hr

Beta irradiation process was done in the University of Baghdad, College of Science, Department of Physics at Nuclear Laboratory.

3-Result and discussion:

There was only one way to disposal from nuclear waste it was stored until it decay to be safe through long term of time and until this time must keep it away from our environment by immobilize it. So in our research, we focused on the effect of Beta radiation on the samples to find determine the true real relationship between effect of radiation on the physical properties (structure properties) of CNTs, to stimulate the change and how much damage that caused by radiation on the microstructure of CNTs. The second benefit of this research is to find a new way to reduce the volume of nuclear waste by converting it to a nanomaterial's.

The effects of radiation on the carbon nanotubes related by the net damage in carbon nanostructure which depends on the energy and radiation types, as well as on the total dose. It is believed that the chemical bond strengths in the already carbon network in are somewhat strong to be destroy or overcome by the higher energy due to -irradiation.

The effect of Beta irradiation on the surface and textural variation are investigated by using X-ray diffraction analysis (XRD) and scanning electron microscope (SEM). XRD and SEM examined at Kashan University by sending samples through a private scientific office (Chemistry Analysis Center (CAC)).

3.1-CNT-NPs Characteristics:

The structure and morphology of prepared CNTs were studied by using SEM. Also, the chemical composition of the synthesized NPs samples was determined by energy dispersive spectroscopy (EDS) measurement. The SEM images and particle weight distribution for CNTs shown in figure 3.

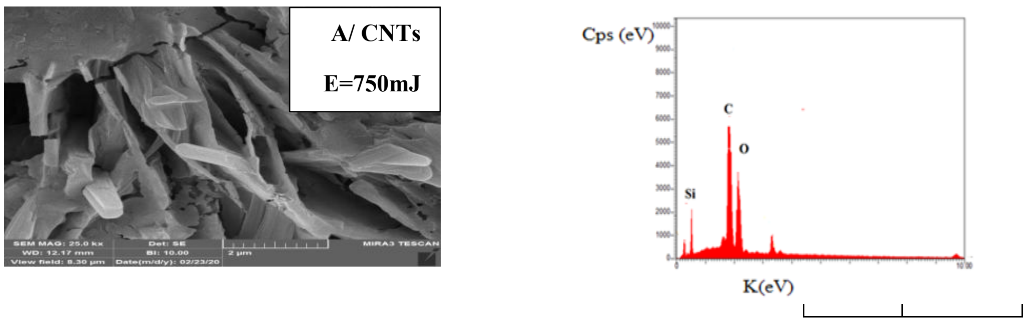


Fig (3): A. SEM image for CNTs at laser 750mJ and no. of pulses 100pulse and B. EDS spectrum with weight percentage of elements in carbon nanotubes sample.

It was found from SEM image that carbon nanostructures that prepared at laser energy750mJ, have a tube shape with some embedded spherical nanoparticle. The nanoparticles size was in the range 15-25 nm. The energy of laser was one of the significant parameter that responsible on the Type of carbon structure that prepared by laser ablation. The mechanism of nano-tube generation in laser ablation of graphite sample in DDW began by photo-thermal operation. Then target temperature increased due increase the number of pulses leading to melting and finally ejected of ablated amount from the target. At the graphite, this caused ejection of multiple or single layers of target. The strong confinement of plasma because of liquid will wholly change all the dynamic of expansion laser ablated materials. So, shockwave with high pressure will generate through both the target and the liquid environment. Because of a high-temperature and pressure, generate high cavitation bubbles inside the liquid. These bubbles expanded and shrink to play an important effect in the structure type and nature of the final ablation output [10]. The figure (3), display the chemical composition of colloidal by using energy dispersive spectroscopy. The interaction of the elements inside solution depends on the interaction between structures of the target sample and the source of excitation. The results of graphite target showed the existence of C, O, and Si related to glass plate elements.

3.2- X-ray diffraction (XRD):

The examination by X-ray diffraction (XRD) is used to characterize the crystal composition, grain size, and preferring orientation in polycrystalline or powdering solid samples. To analysis amorphous phase or crystalline phase for the carbon nanotubes, which contains strontium hydroxide nuclear waste x-ray diffraction device was applied. The data of X-ray diffraction were recorded by using Cu Kα radiation with wave length (1.5406 A) and the intensity of data were calculated between 2θ at the range (20–80) degree.

For all samples the XRD shows there is an appearance of the peaks in the spectra indicates the presence of the crystalline phase which is Strontium Carbonite. It is clear from XRD spectra for all samples the location of the peaks was not affected by increasing the radiation dose and the higher peaks, it's almost appearance at $2\theta = 25$ degree significance the phase of material not change as shown in the figure [4,5 and 6]. In other words, the absence of a new substance, i.e. the immobilization material represented by carbon nanotube is not affected by radiation.

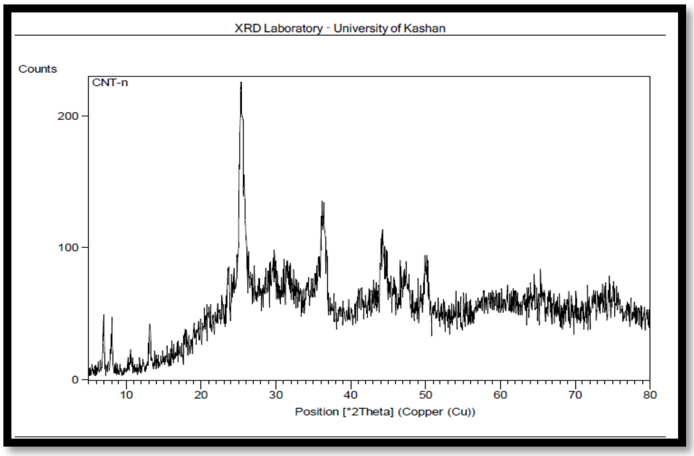


Fig (4): X-ray diffraction CNTs-$Sr(OH)_2$ before exposure to βradiation

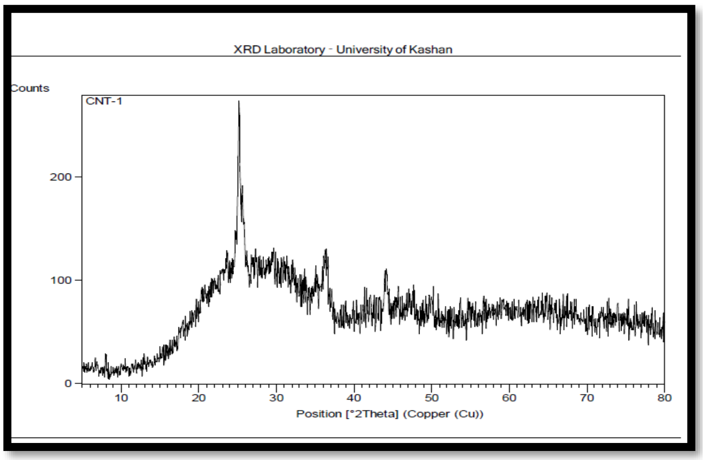


Fig (5): X-ray diffraction CNTs-$Sr(OH)_2$ after exposure to1hr βradiation

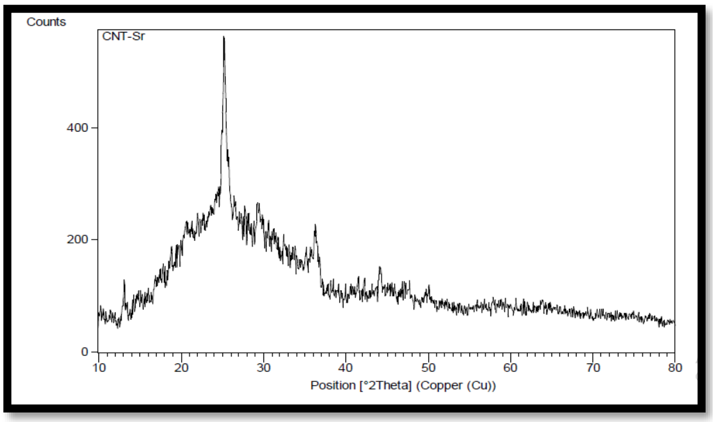


Fig (6): X-ray diffraction CNTs-$Sr(OH)_2$ after exposure to *720 hr β*radiation.

The appearance of Strontium carbonite phase in the XRD its return to the nature of Strontium hydroxide. Due to the nature of Strontium hydroxide its transformation to strontium carbonite because Strontium hydroxide absorb carbon dioxide from the air.

The most important specifications of Strontium carbonate is: white, odorless, tasteless powder. Being a carbonate, it is a weak base and therefore is reactive with acids. It is otherwise stable and safe to work with. It is practically insoluble in water (1 part in 100,000). The solubility is increased significantly if the water is saturated with carbon dioxide [11].

3.3- Scanning electronic microscope (SEM):

The Scanning electronic microscope is utilized to study the morphology of the carbon nanotubes surface which contains strontium hydroxide as a nuclear waste before and after irradiation to reveal the possible textural transformation by radiation. The SEM device is ARYA Electron Optic that operating at 15 kV, beam current 10.000nA, and magnification 12500**.** The SEM micrographs of samples at different magnification figure [7, 8 and 9] shows the formation of Carbon nanotubes that prepared using laser ablation method. Moreover, it was found that CNTs-$Sr(OH)_2$ are well decorated on CNTs surface. And SEM micrograph for samples before and after Beta irradiation show not affected the carbon nanotubes structure by Beta radiation (no destroyed in structure) and the nuclear waste $Sr(OH)_2$ immobilized on the surface of the Carbon nanotubes . Although, there is a slight change the diameters of nuclear waste, the diameter increase with increased radiation exposure time but, the average diameter still at 20 nm and this not influence on the stability of nuclear waste on Carbon nanotubes.

In all three SEM micrograph, CNTs-$Sr(OH)_2$ were well decorated on the surface of CNTs and there was not any remarkable difference in the corresponding due to Beta radiation exposure. These results confirm that the SEM micrograph Fig 5,6 and 7 shows that nuclear waste $Sr(OH)_2$ attach to the CNT surface and form CNTs-$Sr(OH)_2$ nano-composites. And the nuclear waste may immobilized on the CNTs surface due to van der Waals interactions.

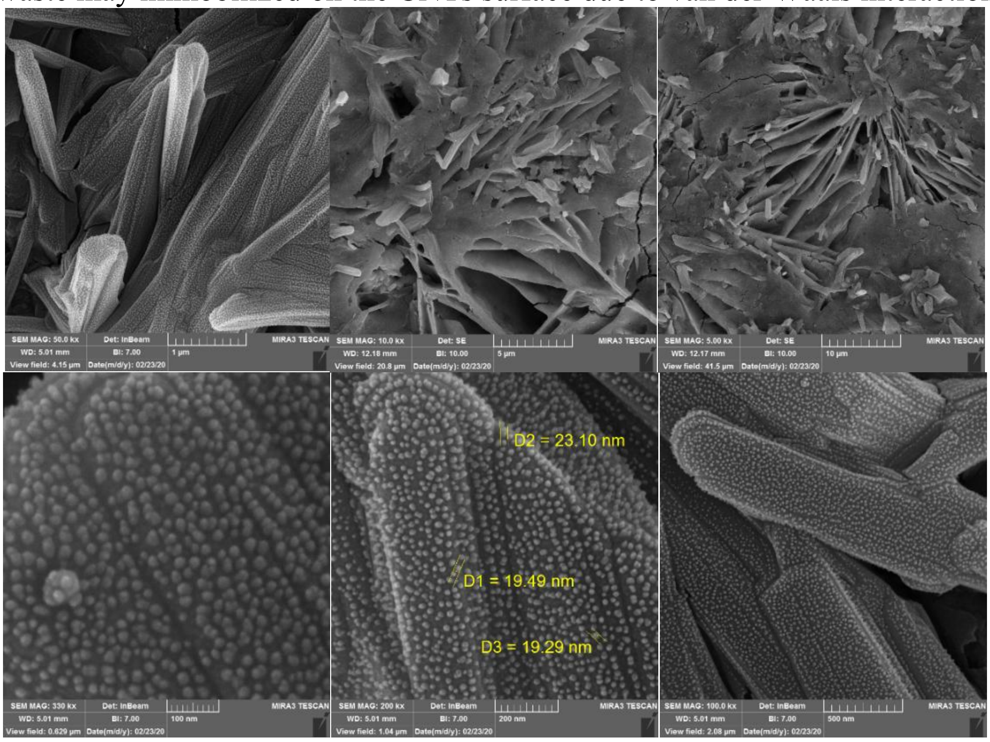


Fig (7): The SEM micrograph for CNTs-$Sr(OH)_2$ sample before exposure to Beta radiation at different magnification.

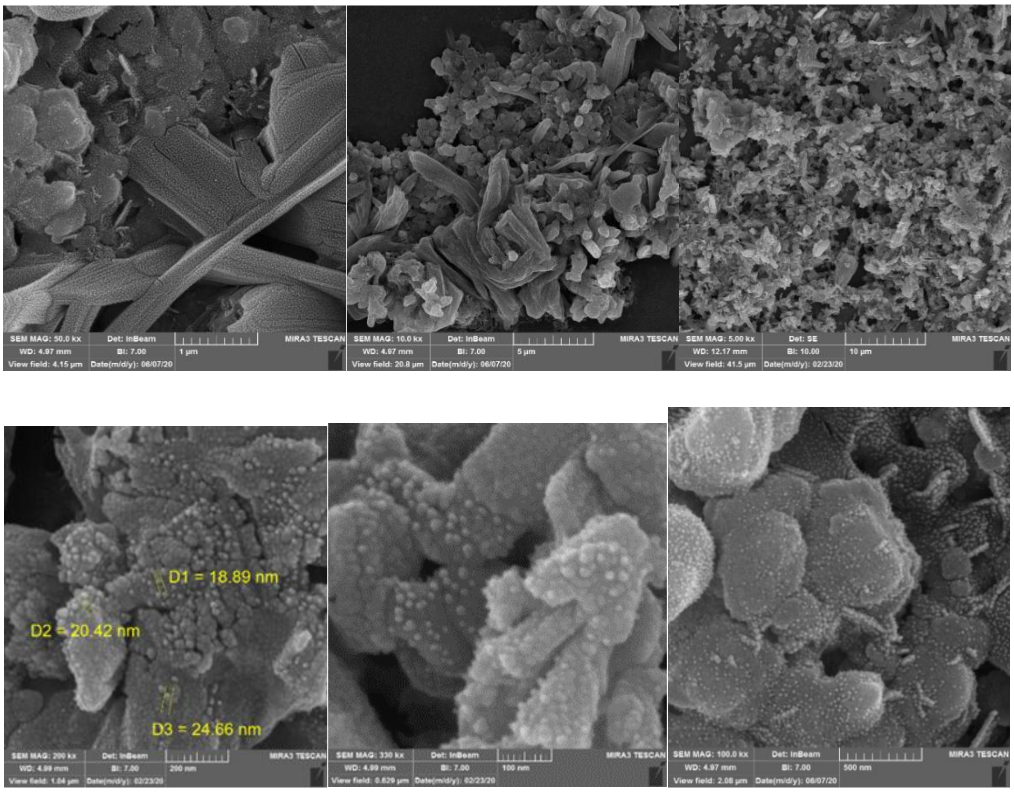
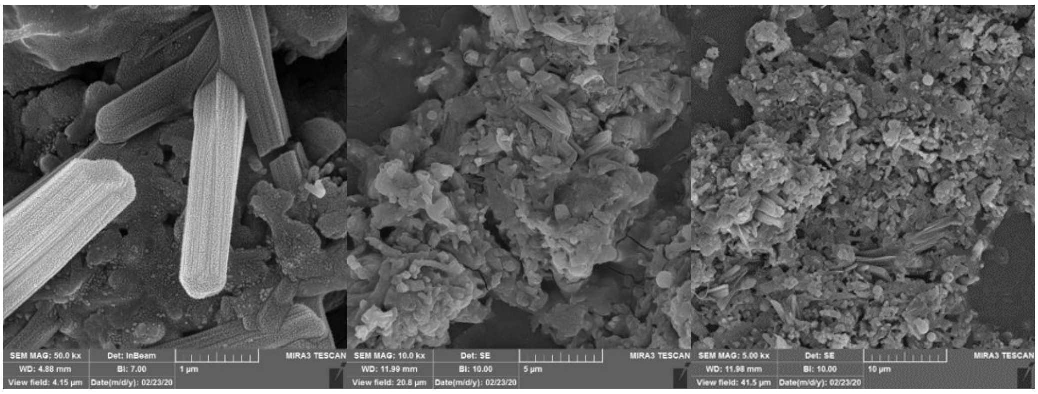


Fig (8): The SEM micrograph for CNTs-$Sr(OH)_2$ sample after exposure to 1 hr Beta radiation



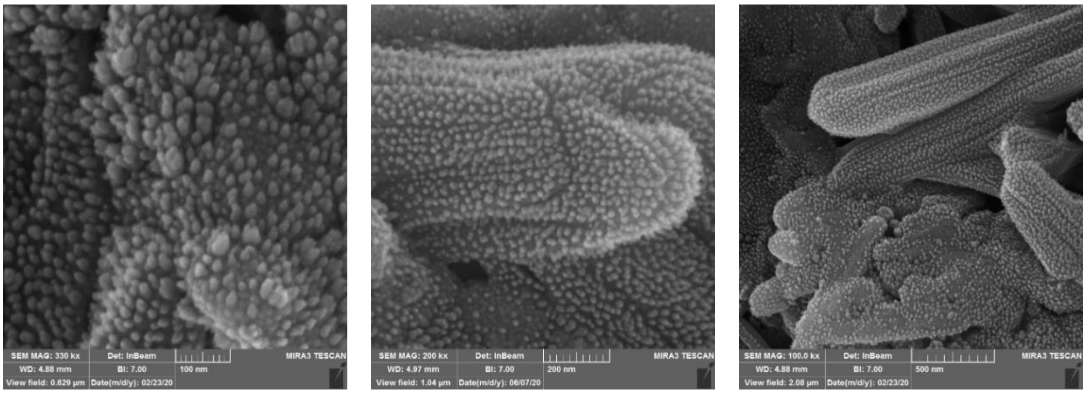


Fig (9): The SEM micrograph for CNTs-$Sr(OH)_2$ sample after exposure to 720 hr Beta radiation

4-Conclusions:

In an attempt to manage the nuclear waste which needs to storage for a long time until loss radiation effect (became safety). Therefore must found a suitable method to immobilize nuclear waste to stop leaching ions to surrounding and pollution environment and threats our health. In this research the nuclear waste (Strontium Oxides) was immobilized by Carbon nanotubes (CNTs). Carbon nanotubes were produced by using laser ablation techniques regard safe, quick and produced at room temperature.

From the X-ray diffraction XRD and scanning electronic microscope (SEM), appears that the carbon nanotubes are a very good material for immobilizing nuclear waste. But, the understanding of the destructive effect of radiation on carbon nanotubes structure has not been reached, partially due to the limited number of studies to date and partially due to the complexities arising from tests with different materials.

References:

[1] Shim HE, Yang JE, Jeong SW, Lee CH, Song L, Mushtaq S, Choi DS, Choi YJ, Jeon J. Silver Nanomaterial-Immobilized Desalination Systems for Efficient Removal of Radioactive Iodine Species in Water. Nanomaterials (Basel). 2018 Aug 26;8(9):660.

[2] Arepalli S. Laser ablation process for single-walled carbon nanotube production. J. Nanosci. Nanotechnol, 2004;4:317–325.

[3] Gao Z, Varela JA, Groc L, Lounis B, Cognet L. Toward the suppression of cellular toxicity from single-walled carbon nanotubes. Biomaterials Science, 2016;4(2):230–244.

[4] Belloni F, Kütahyali C, Rondinella VV, Carbol P, Wiss T, Mangione A. Can carbon nanotubes play a role in the field of nuclear waste management? Environmental Science & Technology,2009;43(5):1250–1255.

[5] Rashid MHO, Ralph SF. Carbon Nanotube Membranes: Synthesis, Properties, and Future Filtration Applications. Nanomaterials, 2017;7(5): 99.

[6] S. Alexander, et al. Preparation and properties of polymer-wrapped single-walled carbon nanotubes. Angewandte Chemie, 2001, 113.9: 1771-1775.

[7] Bull PS. Removal of strontium and cesium from radioactive waste waters by coagulation-flocculation of ferric hydroxide. MSc thesis, University of New South Wales 1974.

[8] Ojovan MI, Lee WE. An introduction to nuclear waste immobilisation. Amsterdam. Elsevier. 2005.

[9] Favrea G, Brennetota R, Chartiera F, Vitorge P. Understanding reactions with O_2 for ^{90}Sr measurements by ICP-MS with collision-reaction cell" International Journal of Mass Spectrometry 2007;265(1):15-22.

[10] Escobar-Alarcón L, Espinosa-Pesqueira ME, Solis-Casados DA, Gonzalo J, Solis J, Martinez-Orts M, Haro-Poniatowski E. (2018). Two-dimensional carbon nanostructures obtained by laser ablation in liquid: effect of an ultrasonic field. Applied Physics A, 2018; 124(2):1-7.

[11] MacMillan JP, et al. Strontium and strontium compounds. Ullman's Encyclopedia of Industrial Chemistry, 2000.