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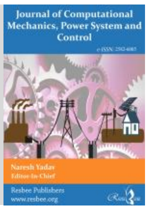

Application of Multi-Walled Carbon Nanotubes based Materials in Heavy Metals Adsorption

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Abstract Rapid population growth and lack of access to safe and clean potable water have recently been of major global concerns. The bioaccumulation of the substantial water contaminants in the living cells brings genuine health issue to the human and generates significant environmental impact. Carbon Nanotubes (CNTs) is one of the advanced technologies recently applied for the wastewater treatment due to outstanding and diverse physio-chemical properties offered by CNTs. The large surface area, flexibility in number of activated functional groups, reasonable adsorption behavior in water, and excellent removal efficiency of heavy metals are of those properties which introduced CNTs as a unique adsorbent. In this work the adsorption behavior of metal ions using Multi-Walled CNTs (MWCNTs) was investigated to detect and evaluate the capacity for Cobalt (CO) and Nickel (Ni) on MWCNTs. A multiple characterization techniques were applied such as Scanning Electron Microscope (SEM), Ultraviolet-Visible Spectroscopy (UV-VIS), Energy Dispersive Spectroscopy (EDS), Raman spectroscopy and Fourier Transformer Infrared (FT-IR) on the samples to illustrate the morphology and composition changes, also to locate defects, porosity, and structure changes of the sample. FT-IR spectrum shows the existence of carboxyl group after treatment with (Acidic oxidation). SEM micrographs show the occurrence of surface modification on the MWCNTs structure after treatment. The results show that CNTs are excellent and effective adsorbent for eliminating harmful media in water. Both heavy metals are strongly dependent on pH, oxidized MWCNT concentration and ionic strength. Oxidized MWCNTs may be a promising candidate for concentration of heavy metal ions from industrial wastewater.

Keywords: MWCNTs, Oxidization, Wastewater Treatment, Adsorption, Heavy Metals.

1. Introduction

Along with the rapid grow in industrialization of human society, industries release different sorts of contaminants into wastewater, including heavy metal ions, bacterial contaminations, viruses, hazardous organic compounds, etc., which bring serious health issues to the human. Among entire water contaminations, the heavy metal ions including Pb2+, Zn2+, Hg2+, Cd2+ and Ni2+ possess high level of toxicity; they are non-biodegradable and can result in severe health issues in human beings and animals [13]. In 1676 Van Leeuwenhoek observed the first microorganisms, therefore in first beginning of the eighteenth century the application of water filters came to life, it was made from wool, sponge and charcoal. The home of wastewater treatment revolution was in Scotland; in 1804 an actual water treatment plant was built and designed by Robert Thom, and this great move helped people in Europe to get access to clean drinking water. A tremendous leap is achieved during the last two centuries in wastewater treatment field, nowadays the treatment becomes more advanced, well easily operated and most important the results are guaranteed. Different techniques are provided to treat wastewater in present days, but of course each one of them is carrying some limitation either technical or economical. Since wastewater contains different kinds of waste in a micro-scale and in a visible scale therefore different approaches and techniques are used, for example filtration method is used to separate the solid particles from the effluent, and it is quite similar to screening process that is used to remove largest objects from waste water [14]. To go deeper, Reverse Osmosis (RO) is used in both areas industrial and potable water, and it is the usage of a semipermeable membrane that allows small particles to pass through the membrane by creating reverse pressure on both sides of the membrane, and of course large objects will remain inside the membrane's pores. Distillation also used to separate unwanted components

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by selective evaporation and condensation [5]. The adsorption techniques have captured the world's attention due to its sufficient removal, low cost and free complexity steps. There are many materials which can be utilized for adsorption purpose. In the beginning of this trend, metal oxides and some carbonaceous materials such as activated carbon were used, but due to their low absorbance capacities the researchers attempted to find other alternatives for those conventional materials [15]. In recent years, nanotechnology has introduced different types of nanomaterials to the water industry that can have promising outcomes [10]. CNTs amongst nanomaterials have attracted much interest due to their novel optoelectronic applications such as flat panel displays, chemical sensors, ultra-sensitive electromechanical, energy and hydrogen storage devices [6] [16]. In addition, the CNTs applications for the removal of hazardous pollutants from industrial gas and aqueous solutions streams have been extensively studied. This is due to their large specific surface area, highly hollow and porous structure, light mass density to be able to strongly interact with pollutant molecules and help with their removal [4]. The other perspective to look at CNTs as adsorbents would be from their high chemical selectivity benefiting the wastewater filtration mechanism through chemical interactions and size exclusion when sorbate molecules flow either on their outer surface or along their inner walls [12] [17]. It is noteworthy that subsequent functionalization of the CNTs surface with chemically active species could endow them with further physio-chemical selectivity. A number of studies have already been carried out to remove heavy metals [8] in wastewater treatment using single-walled CNTs (SWCNTs) [7] and MWCNTs [9]. CNTs have been used as Nano sorbents separately, and demonstrated high efficiency rate in adsorbing of divalent metal ions [18].

Pyrzynska and Bystrzejewski [19] provided information with regards to the pros and cons of using carbonaceous materials [11] (i.e CNTs, activated carbon and carbon-encapsulate magnetic nanoparticles) for heavy metals adsorption via studying the adsorption of Co2+ and Cu2+ on their surface [8]. Their experimental results demonstrated that carbon-based nanomaterials have significantly enhanced the adsorption efficiency in comparison with activated carbons. Furthermore, modification of the CNTs surface with by oxidation, combing with other metal ions or metal oxides and coupling with organic compounds have exhibited enhanced adsorption capacities.

In a molecular dynamic simulation study, Anitha and co-workers [3] investigated the adsorption behavior of divalent metal cations (Cd+2, Cu+2, Pb+2, and Hg+2) on a CNT surface [1]. They have calculated the normalized radial density profiles of metal ions with and without presence of functional groups (such as −COO–, –OH, and −CONH2) on CNTs surface. They have also found that the adsorption kinetic mostly followed the Langmuir isotherm model [2]. The maximum adsorption capacities of the heavy metal ions were found in the following order: Pb2+ > Cu2+ > Cd2+ > Hg2+. Also it was resulted that CNTs with functionalization of carboxylic group (−COO–) act a better adsorbent in comparison with other functional groups (−OH and −CONH2). CNTs could be synthesized in laboratory by three different methods, which are Laser ablation, Arc discharge and Chemical Vapor Deposition (CVD), and the last method is the most used one. One of CNTs features is that they are hydrophobic; therefore, it is hard to disperse them into water or aqueous solution. Oxidation method help in the dispersion process of CNTs. Functional groups like carboxyl and hydroxyl will be attached to carbon atoms after oxidation, also its separate the tubes and to not let them aggregate as one bundle of tubes. During performing the oxidation method, it is considered as critical step because, a wrong procedure in doing oxidation to CNTs might damage the tubes or even create defects to them, in some cases it might affect CNTs diameter or length, in worst cases we might end up losing the whole material. The oxidation procedures are very simple, it is mainly addition of acids in a correct quantity, mostly it is common to use nitric acid (HNO3), hydrochloric acid (HCL) and sulfuric acid (H2SO4) or even mixture of three of them. The affinity of heavy metal ions towards CNTs can be affected by several factors such as, PH level of the solution and impurity of the sample. For PH level an acidic treatment will lead to a decrease of the PH level and that will change the preferences of the adsorption behavior it might show some ups and downs on the UV spectra [8]. Also, if a CNT sample contains some impurities from the syntheses of CNT or catalyst insignificant impurities; this will affect the adsorption behavior.

The aim of this research paper is to provide experimental results of using MWCNTs for heavy metal ions removal from wastewater which is from an environmental point of view a very powerful technique in wastewater treatment. The prime objective of the present work is aimed to investigate the following:

To oxidize MWCNTs by acidic treatment to convert the material into hydrophilic material.

To characterize MWCNTs and O-MWCNTs with different techniques like SEM, UV-VIS and FT-IR.

To investigate the heavy metal adsorption behaviour of MWCNTs.

2. Experimental Methods

2.1 Oxidation of MWCNTs

To prepare Oxidized MWCNTs (Ox-MWCNTs), a well common method is used. MWCNTs (2.0g) were dispersed in 700 ml of concentrated H2SO4/HNO3 mixture (V: V 3:1) and sonicated in a bath sonicator for 70 minutes. Then, cooled at room temperature. Followed by repeated washing with deionized water to reach neutral PH level and to ensure all impurities were removed. Washing process were accomplished with the help of centrifuge that in every batch of washing the precipitated MWCNTs were collected and the supernatant was discarded then dried in oven at 60˚C overnight (24h) to ensure complete dryness.

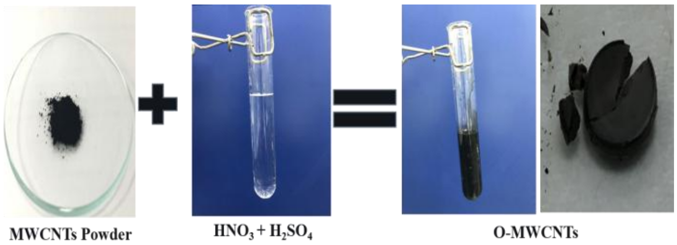

Fig. 1. *Oxidation of MWCNTs.*

2.2 Adsorption Study

The adsorption of heavy metal ions on MWCNTs has been discussed more often; our results might stick to the adsorption mechanism. Due to the porous structure or surface of MWCNTs the adsorption of heavy metal ions will occur inside these pores, and the important role that oxidation process does is to create functional groups on the surface of MWCNTs, these groups will increase the capacity of adsorption by changing some physiochemical property which is the hydrophobic property of MWCNTs in water or aqueous solution, into hydrophilic property. Before oxidation of MWNCTs they were hydrophilic and they tend to stick to each other and aggregate as one bulk, but after oxidation they turn into hydrophilic and they have the ability to be dispersed in water or aqueous solution. The dispersion of MWCNTs will increase the surface area of each tube therefore the adsorption capacity will increase. For our experiment the centrifuged samples prepared in the previous stage were used for the heavy metal adsorption studies by utilizing the UV-VIS spectroscopy. The adsorption behavior of Co and Ni ions on synthesized O-MWCNT from the previous stage was investigated individually. 0.8g of O-MWCNT used in individual heavy metal adsorption, placed in the cuvettes containing 3 mL of heavy metal solutions of 12 mM concentration.

3. Characterizations of CNT

Since CNTs possess a unique structure, with different types and arrays, with variety of physiochemical properties and without forgetting the Nano scale measurement. Therefore, they require a higher attention in terms of characterization and analysis, to discover the topography and morphology of the material, and to see the shape and forming structure of the material for better understanding. In this study the samples after preparations were characterized in two different stages, one stage is before oxidation which was powder CNT (MWCNTs), the other stage was after oxidation process using aqua regia method (O-MWCNTs). The morphologies of the nanotubes were characterized using SEM at different resolutions. The energy dispersive X-ray spectroscopy (EDS) on the same SEM instrument was used to carry out the overall and individual elemental mapping to determine the various elements that the samples contained. Fourier transform infrared spectroscopy (FT-IR) analysis were conducted in transmittance mode via JASCO FT/IR 6300 in order to investigate the vibrational stretching of different bonds, including oxygen functional groups before and after oxidation process. Raman spectroscopy were done using RENSHAW Raman Microscope which has an important role to characterize the graphitic structure including the degree of the graphitization as well is presence of the defects. Also, the strength of adherence of various functionalities to the surface of CNTs can be monitored by this spectroscopy. Finally, Ocean optic UV-Vis kit was used in order to investigate the heavy metal adsorption behavior of the O-MWCNTs.

4. Results and Discussion

4.1 Heavy Metals Adsorption Study

The adsorption behavior of heavy metal ions on O-MWCNTs has been extensively described. As shown in Fig. 2 O-MWCNTs adsorb heavy metals individually, starting with Co and then Ni effectively. Each heavy metal adsorption process is kept overnight in UV-VIS spectroscopy supplied by ocean optics. The concentration of heavy metal plays a critical role along with the PH level and the acidic residues after oxidation process. At high concentration, the adsorption capacity gradually increased reaching to high range of adsorption, indicating full-occupied adsorptive sites of O-MWCNTs. Adsorption results shown in figures below. In Fig. 2 R2 is 0.9387, which is close to 1 the adsorption occurs at its maximum. Fig. 3 Indicates the removal of Ni form wastewater using O-MWCNTs, the R2 with value of 0.8825, which is less adsorption capacity compared with Co removal.

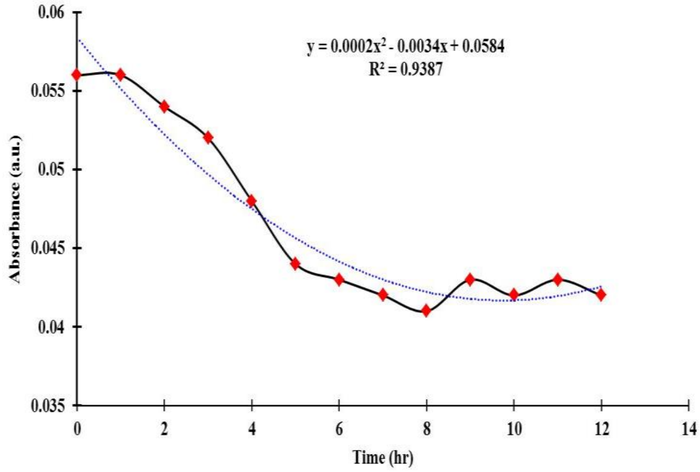

Fig. 2. *Cobalt removal using O-MWCNTs*

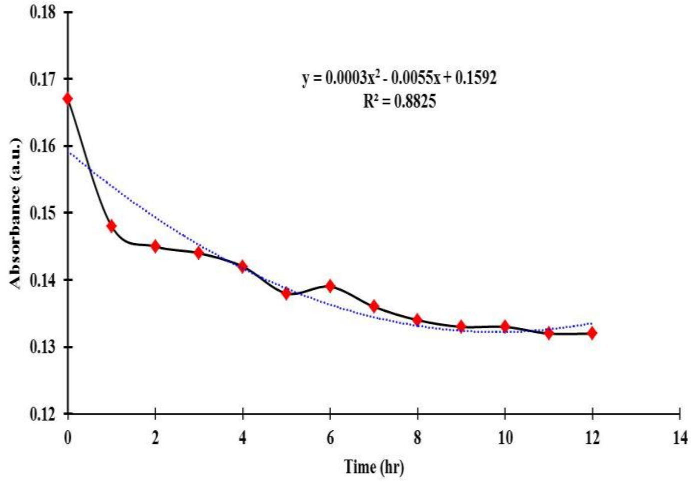

Fig. 3. *Nickle removal using O-MWCNTs.*

4.2 Colloidal Stability Of CNT Suspensions

It is well known, CNTs have a strong tendency to agglomerate due to their Nano size and their respective high surface energy. However, the grafting of chemical functionalities on the CNT surface, such as carboxylates, imparts negative charges and therefore, creates the electrostatic stability required for a colloidal dispersion. This is indeed confirmed since the chemical treatments applied, were found to improve the dispersion stability of CNTs.

4.3 FT-IR Result Of Mwcnts Before and After Oxidation

Fig. 4 Shows the FT-IR spectrum of the sample, characterized in two different stages one stage before oxidation (Raw-MWCNTs), other stage was after oxidation process (Ox-MWCNTs). This clearly confirmed that there are no functional groups on the pure MWCNTs while Ox-MWCNTs exhibited numbers of those peaks in the wavenumber range 500 to 4000 (cm-1), which attribute to the existence of some functional groups. Hydroxyl -OH stretching at 3381 cm-1, carboxyl C=O at 1720 cm-1, the in-plane C=C (sp2 carbon) skeletal stretching vibrations at 1616 cm−1, Hydroxyl bending at 1485 cm-1, epoxy C-O at 1145 cm-1 and C-O Alkoxy were identified in the Ox-MWCNTs graphitic surfaces. The appearance of these peaks in Ox-MWCNTs spectra indicates a significant oxidation of nanotubes surfaces.

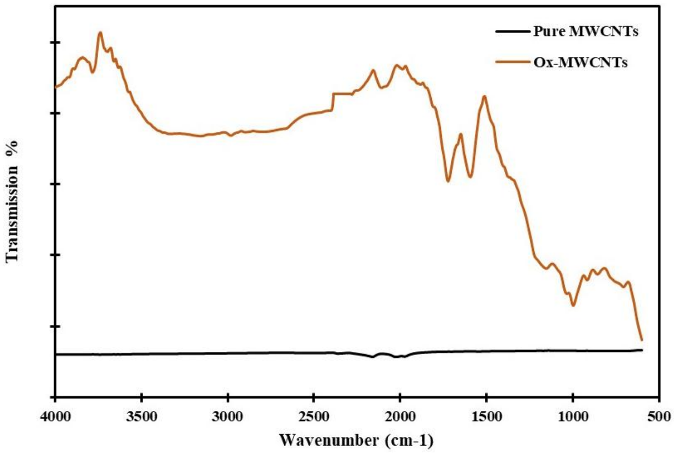

Fig. 4. *FT-IR spectrum for pure and oxide MWCNTs*

4.4 Raman Spectroscopy

Raman spectra, used to observe the fingerprints of a sample to determine the chemical structure and identify molecules whether it is a pure MWCNTs or it contains other impurities form pervious processes which can be observed by peaks generated by molecules vibrations. Fig. 5 represents MWCNTs and spectra of O-MWCNTs characterized by the occurrence of the following bands:1357 cm-1 (D band corresponding the structural defects of MWCNTs), 1584 cm-1 (G band corresponding the degree of MWCNTs graphitization). Analyzing the shape an intensity of the peaks at D and G bands (the intensity ratio of ID/IG) before and after oxidation provide us with information about the molecular structure change after oxidation process interestingly the ID/IG ratio for both MWCNTs and O-MWCNTs are about 0.64 which evidences that the acid treatment of MWCNTs could not cause any impact on the bonding structure of the nanotubes.

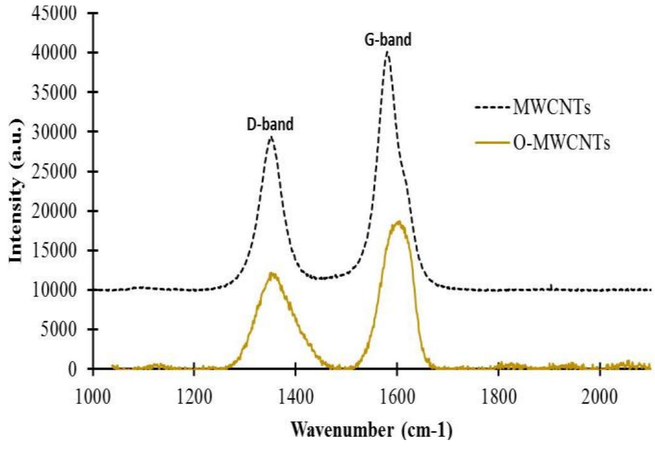

Fig. 5. *Raman spectra indicate MWCNTs and O-MWCNTs D, G peaks.*

4.5 Electron Microscopy

Scanning electron microscopy was used to investigate possible MWCNTs fragmentation occurred during treatment and used to detect possible morphological changes on MWCNT specimens depending on the severity of treatment. Fig. 6 shows a low magnification image of the raw-MWCNTs sample in powder form, the images were taken in different scales to illustrate the raw-MWCNTs more obvious. The images determine that the powder sample as received is agglomerated and aggregated on each other, and in this form of stacking of the tubes they cannot be dispersed in aqueous solutions, because in this form they tend to be hydrophobic and in order to disperse them you need the acidic treatment (oxidization). Figures 7 illustrate more clear picture of the tubes morphology by magnifying the resolution.

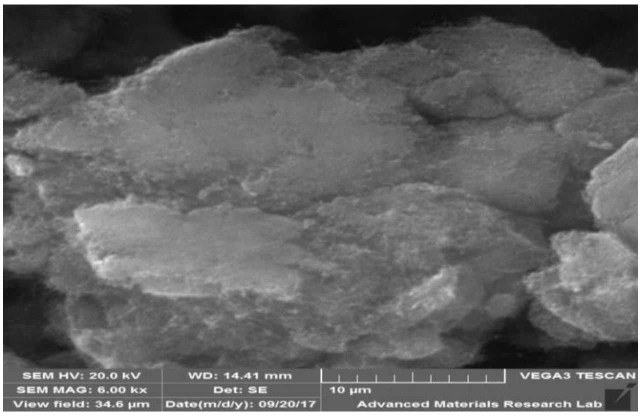

Fig. 6. *6kx magnification SEM image of raw-MWCNTs powder.*

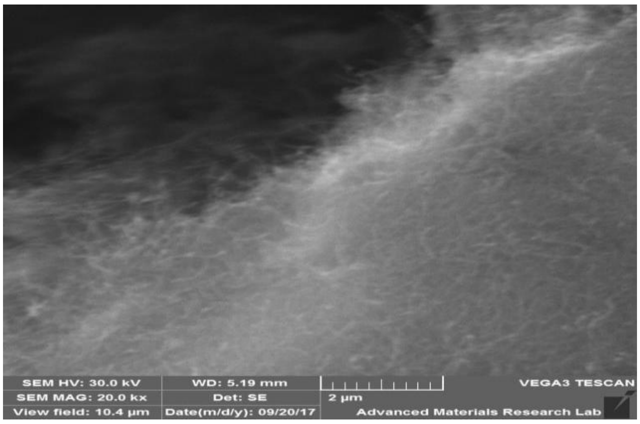

Fig. 7. *20kx magnification SEM image of raw-MWCNTs powder.*

4.6 EDS For RAW-Mwcnts

EDS was conducted using SEM. EDS used to detect the different elements in the sample, either overall mapping of the sample as in Fig. 9 or individual mapping for each element that present in the sample as in Fig. 10, at 10m measurement which show the distribution of each element across the selected region of the MWCNTs sample. Fig. 8 Indicates that Carbon is the highest percentage in CNTs sample with 95%wt, followed by 2.9%wt Oxygen and small quantities of Ni, Cu, Fe and S. This indicates that the sample is not full pure it contains some impurities, and this impurity is due to the synthesis method of the sample and the purification of the sample as a post process after synthesis of the CNT.

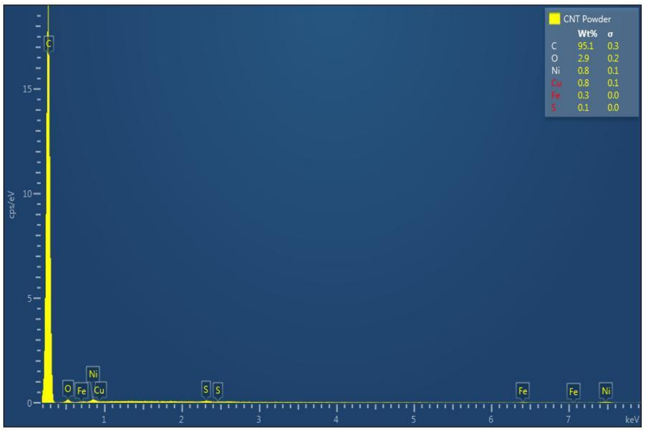

Fig. 8. *EDS overall mapping graph with element's percentage of CNT powder*

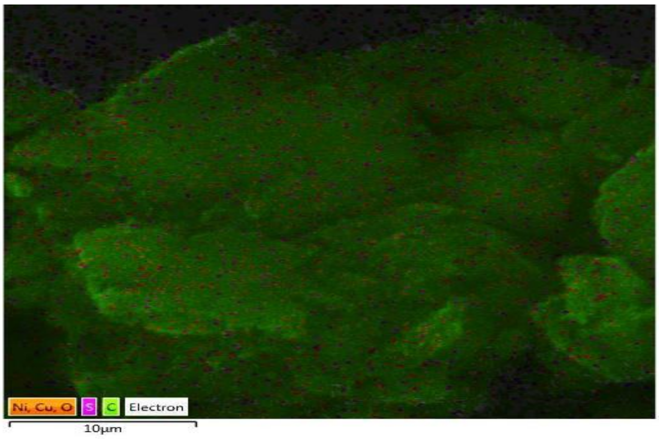

Fig. 9. *EDS mapping of raw-MWCNTs powder represents overlap of all elements*

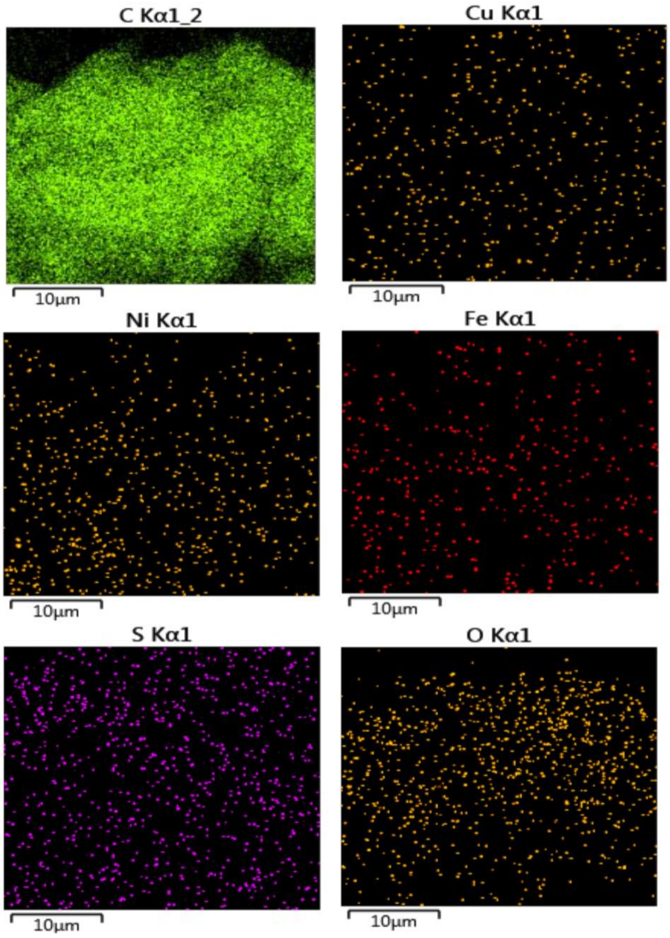

Fig. 10. *EDS mapping of raw-MWCNTs powder for each individual element at 10μm measurements.*

4.7 SEM Images For O-MWCNTs

After characterization of the raw sample of CNTs, a comparison is required to determine the changes occurred on the sample due to the acidic treatment. The images illustrate some changes, the sample had the trend to be dispersed in aqueous solutions, therefore the tubes are dispersed and the adsorption capacity increases as the surface are of the tubes increase. Different resolution scales used to magnify the images for better illustration as represented in figures below:

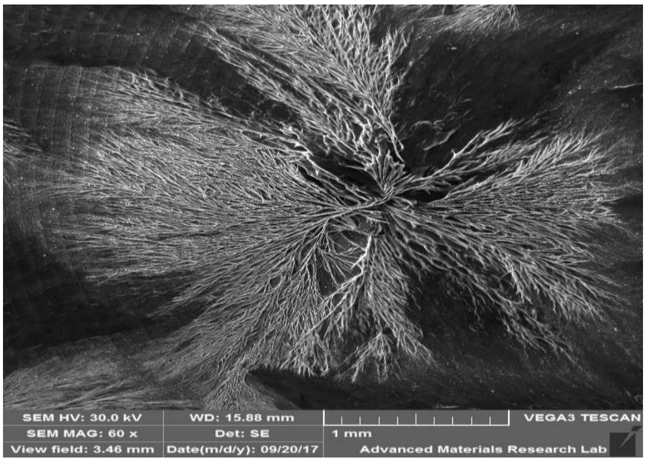

Fig. 11. *Low magnification (60x) SEM image of O-MWCNTs*

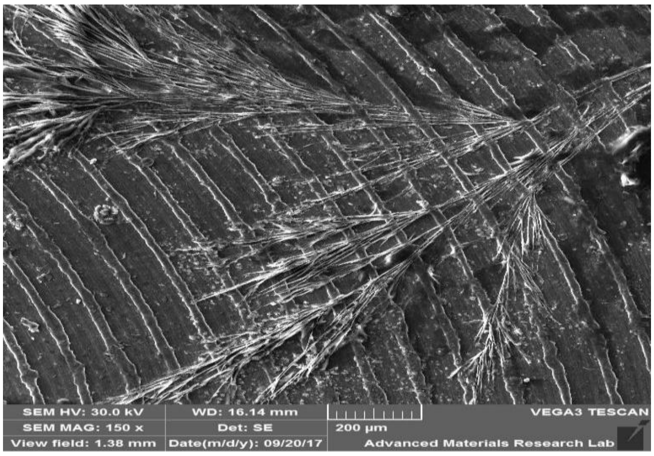

Fig. 12. *150x magnification SEM image of O-MWCNTs*

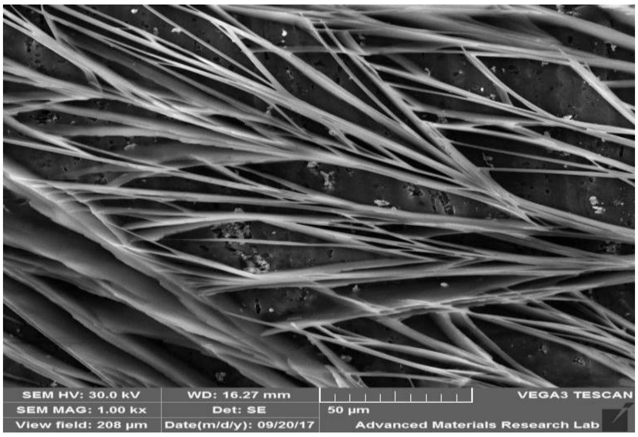

Fig. 13. *1kx magnification SEM image of O-MWCNTs (site 1)*

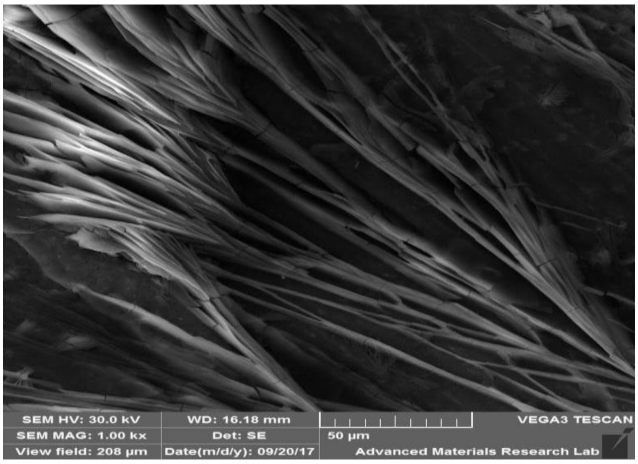

Fig. 14. *1kx magnification SEM image of O-MWCNTs (site 2)*

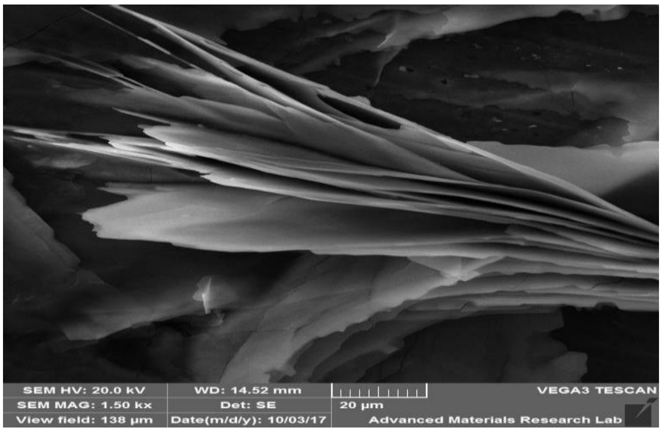

Fig. 15. *1.5kx magnification SEM image of O-MWCNTs*

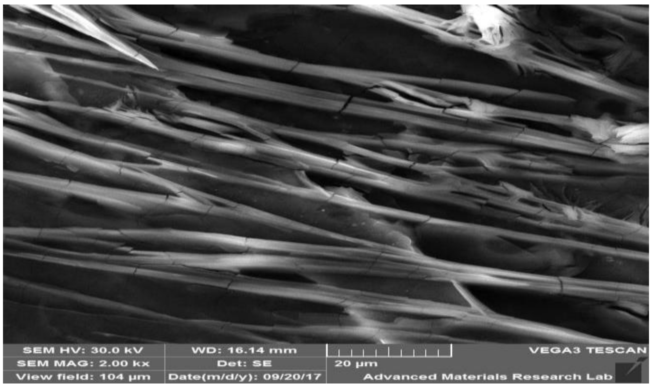

Fig. 16. *2kx magnification SEM image of O-MWCNTs*

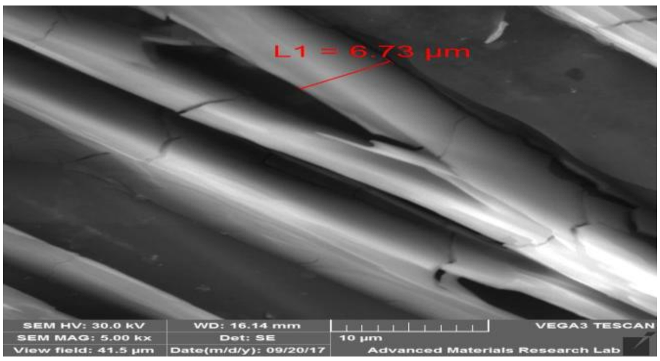

Fig. 17. *5kx magnification SEM image of O-MWCNTs showing the outer diameter*

4.8 EDS for O-MWCNTs

Fig. 18 shows overall mapping of all elements and Fig. 19 shows the individual mapping for each element, at 50 m measurement which show the distribution of each element across the selected region of the CNTs sample. In qualitative comparison with the mapping of the pure MWCNTs, oxygen atoms (shown in orange color) were highly spotted in O-MWCNTs.

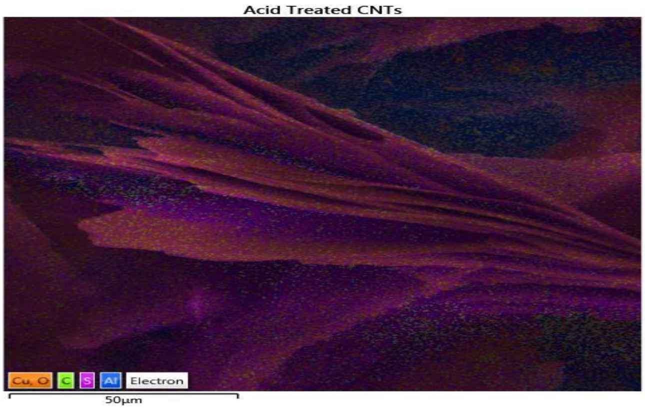

Fig. 18. *EDS mapping of O-MWCNTs powder show overlap of all elements*

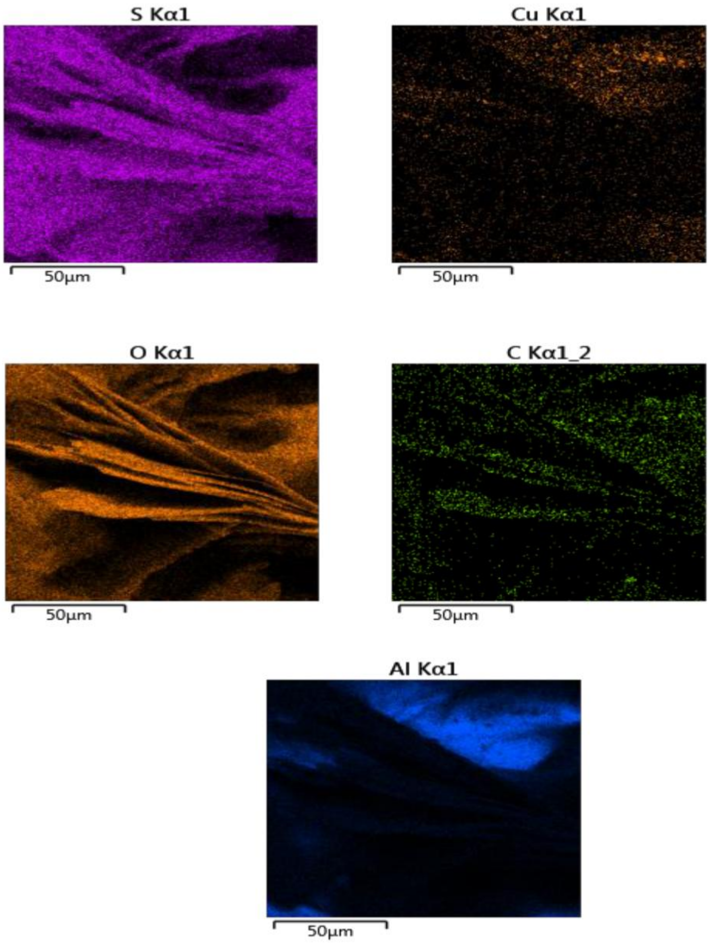

Fig. 19. *EDS mapping of O-MWCNTs powder represents each individual element at 50µm measurements*

Fig. 20 shows an EDS overall mapping graph of the percentage for different elements in O-MWCNTs indicates the changes in amount of each element after acidic treatment. In comparison of CNTs powder sample the percentage of Oxygen increased and the Carbon presence decreased due to the formation of the Oxygen functional groups of O-MWCNTs.

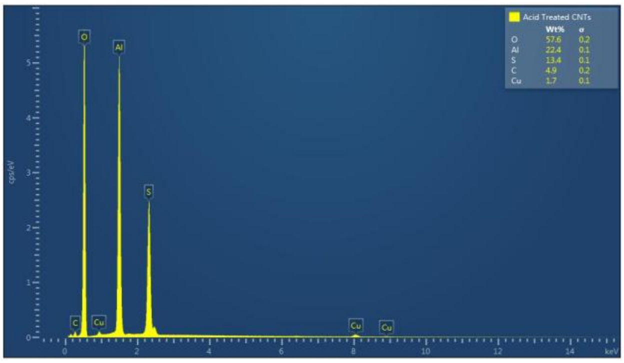

Fig. 20. *EDS overall mapping graph with element's percentage of O-MWCNTs*

5. Conclusion

In summary, CNTs were oxidized with concentrated acidic mixture of Nitric acid and Sulfuric acid, at room temperature and then sonicated and centrifuged to get O-MWCNTs. The results showed a great adsorption capacity towards heavy metal ions, especially after acidic treatment, the adsorption behavior was demonstrated using UV-VIS spectroscopy, and the characterization analysis was carried out by using SEM, EDS, FT-IR and Raman spectroscopy. The adsorption was investigated on two types of heavy metals individually Co and Ni, to define which of the two selected heavy metals is having the highest adsorption capacity. FTIR spectrum shows the existence of carboxyl group after treatment with (Acidic oxidation). SEM micrographs show the occurrence of surface modification on the MWCNTs structure after treatment. The results show that CNTs are excellent and effective adsorbent for eliminating harmful media in water. Both heavy metals are strongly dependent on pH, oxidized MWCNT concentration and ionic strength. Oxidized MWCNTs may be a promising candidate for concentration of heavy metal ions from industrial wastewater.

Future scope

Since CNTs, are considered among the latest advanced materials that have been discovered yet. Therefore, hundreds of applications could be applied on CNTs, also could be completed by deferent batches of researchers. Due to the timeframe that allocated to this work and lack of facilities, some future work needs to be carried out. Investigation of different types of heavy metals should be considered, and more analysis should be applied on the samples in case of different applications will be implemented. X-Ray Diffraction (XRD), Inductive coupling plasma (ICP) and Transmission Electron Microscope should be carried out to characterize the samples. Since the work is concern of removal of heavy metal ICP should be presented to illustrate the adsorbed heavy metal ions in the sample. Further studies will cover the parts of the next stage of the work.

Compliance with Ethical Standards

Conflicts of interest: Authors declared that they have no conflict of interest.

Human participants: The conducted research follows the ethical standards and the authors ensured that they have not conducted any studies with human participants or animals.

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