Carbon Nanotube Filters for Removal of Air Pollutants from Mobile Sources

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Abstract

The aim of this work was the assessment of the removal of air pollutants from mobile sources by commercial carbon nanotubes (CNTs). For this, the nanomaterial was characterized by different techniques: SEM, EDS, TEM, XRD, BET, and Raman. Subsequently, the CNTs were packed in a stainless steel filters which was designed from different prototypes that were developed during the investigation. Tests were performed in the TO-913 Verificenter Macrover Auto SAQ. Inc. de CV. The results revealed that particle type sand CNTs loading had greater effects on the efficiencies than the membrane type sand pore sizes tested. When collecting NO_x, the efficiencies were observed relatively lower, below 20% for loadings of 0.3 - 1.5 mg/cm^2. The studied CNTs were multi-walled: two layers, show a nonlinear growth and morphology varied since they are of different diameters and longitudes, it was observed that half of the nanotubes were coated with amorphous carbon. The composition is mainly carbon and oxygen, iron is also present. The adsorption capacity of CNTs was significantly influenced by the different aspects, like model, brand, fuel, year and the conditions of each car. The removal efficiencies of CNTs filters were shown to range from 10% to 95% in average for the CNTs loadings of 0.2 - 1.6 mg/cm^2. When collecting CO, CO_2, NO_x, HC, the efficiencies were shown to range from 5% to 60% given similar CNTs loadings used.

Keywords

Carbon Nanotubes, NO_x, Air Contamination, Removal Efficiency, Mobile

1. Introduction

The atmosphere is essential for life so their disorders have a major impact on

man and other living beings and, in general, worldwide, the health, environmental, and economic impacts of air pollution are significant [1]. Nowadays, emission of greenhouse gases due to incomplete combustion of fossil fuels which causes global warming is one of the most important environmental problems in the world [2]. Air pollutants, such as carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x), Volatile Organic Compounds (VOCs), ozone (O_3), heavy metals, and respirable particulate matter ($PM_{2.5}$ and PM_{10}), differ in their chemical composition, reaction properties, emission, time of disintegration and ability to diffuse in long or short distances [3].

Gaseous pollutants contribute to a great extent in composition variations of the atmosphere and are mainly due to incomplete combustion of fossil fuels [4]. A major source of air pollution in urban areas is the incomplete combustion of diesel and gasoline fuels in cars, buses, trucks and other on-road transportation sources (aircrafts) [5]. The main anthropogenic sources are mobile and stationary combustion sources. As a result of fuel incomplete combustion, automobiles emit various compounds into the atmosphere in the form of exhaust. Mobile sources have a significant influence on both NO_x and VOC pollution. Nitrogen oxides are emitted as NO which rapidly reacts with ozone or radicals in the atmosphere forming NO_2. Moreover, ozone in the lower atmospheric layers is formed by a series of reactions involving NO_2 and volatile organic compounds, a process initiated by sun light. CO, on the other hand, is a product of incomplete combustion. Its major source is road transport too. A major class of compounds that fuel combustion and especially incomplete combustion processes for energy production and road transport are the major source of emission are the so called volatile organic compounds (VOCs). This is a class of compounds, which includes chemical species of organic nature such as benzene.

The complexity of spatial and temporal distributions of vehicle emissions/ activities and the mobility of vehicles make it very hard to quantify the proportions of ambient air pollutant concentrations attributable to on-road mobile sources [6]. Ambient concentrations of pollutants are correlated with emissions, but the contribution to ambient air quality of on road mobile sources is not necessarily equal to their contribution to regional emissions. This is true for several reasons such as the distribution of other pollution sources and regional topology, as well as meteorology.

Long-term epidemiologic studies have reported an increased risk of all causes of mortality, cardiopulmonary mortality, and lung cancer mortality associated with increasing exposures to air pollution. Adverse reproductive effects (risk for low birth weight) have also recently been reported in Eastern Europe and North America. Daily increments in the concentrations of air pollutants are associated, in the short term, an increase in the number of deaths in cities [7].

For the developing countries there have been few or no monitoring programs to demonstrate the long term development, but in many cases there is indication of a rapidly deteriorating environment [8]. In Mexico, state or local agencies can

have more restrictive standards. The vehicle emissions verification program in Mexico is intended to reduce air pollution emissions from vehicles by ensuring that those vehicles with high emission levels are correctly repaired. In Mexico, to date, only the Mexico City has established extensive standards more restrictive and these only for gasoline powered automobiles. For the gasoline-engine equipped vehicle population, the emissions verification program targets four types of pollution: hydrocarbons (HC), oxides of nitrogen (NO_x), carbon monoxide (CO) and carbon dioxide (CO_2). The vehicle emissions verification program requires the measurement of the vehicles tail-pipe emissions together with various visual checks of the vehicles principal emission control components. The cut-points are established for each contaminant based on two main criteria; the technical feasibility of achieving the desired level of emissions from the different vehicle specifications that are found in the population and the reduction that is required to reach and maintain an acceptable air quality within the city.

For all these reasons it is understood the urgency of seeking alternative technologies to avoid situations arise serious in the life of mankind and the entire biosphere. Sorbent-based processes for gas storage, separation, and purification have been the subjects of many research and studies during the past 50 years. Carbonaceous materials such as active carbon [9] [10] and carbon fiber [11] [12] have widely used in the gas sorption processes. Nanotechnology is nowadays one of the most important trends in science, perceived as one of the key technologies of the present century, its applications are variously. Nanotechnology includes the production of novel and revolutionary materials of the size of 100 nm or even smaller. Carbon nanotubes (CNTs) are part of these novel materials. In the recent years, one of the innovative proposals for controlling pollutant emissions are CNTs due to their distinctive chemical and physical properties like high BET area which enable them to be used in many applications, such as a new type of sorbent for environmental applications [13]-[20]. Recently, nanotube filter was successfully created and utilized to remove the biological agents from the water with filtration efficiency [21] and removing bioaerosols [22]. However, carbon nanotubes filter has not been evaluated in removing air pollutants of mobile sources despite its relevant advantages. In this study, carbon nanotubes filter were prepared by depositing carbon nanotubes on to membrane support of different materials with pore sizes of 10 mm. The removal efficiencies of the CNTs filters prepared were investigated when collecting air pollutants of car exhausts. To our best knowledge, this study report the use of CNTs filter in removing air pollutants of mobile sources and the information provided here is useful both in air pollutants study and air pollution control measures.

2. Experimental Methods

2.1. Material and Method

Commercially available CNTs were provided by the Dr. Carlos Velasco and Dra. Ana Laura Martínez-Hernández from the Applied Physics and Center for Ad-

vanced Technology in the UNAM Campus Juriquilla Querétaro, México. The physical properties of CNTs were obtained using different techniques.

2.2. Physicochemical Characterization of CNTs

The CNTs were characterized after and before that air pollutants sorption process, for techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), X-ray Diffraction (XRD) and Brunauer, Emmett and Teller (BET), most common method used to describe specific surface area to compare the physicochemical differences.

2.2.1. Morphology and Elemental Composition

Scanning Electron Microscopy (*SEM*) was used to determine the morphology of the carbon nanotubes through a scanning electron microscope, model JEOL 5900 LV, at 25 kV. The samples were mounted on an aluminium holder. In all cases, the images were obtained with a backscattered electron detector. Energy X-ray Dispersion Spectroscopy (EDS) determined the semi-quantitative elemental chemical compositions of the samples with an EDAX-4 spectrometer.

Transmission Electron Microscopy (*TEM*) is the most important and reliable technique for correctly identifying the nature and the form of carbon nanomaterials in academic research and in industry. The information provided by TEM directly reveals both the surface and the intrinsic structure of the nanotube [23]. The observation for this research was carried out with a JEOL JEM-2010 TEM operating at 400 kV.

2.2.2. Crystalline Components

Compounds were identified by comparing the diffraction patterns to the Joint Committee on Powder Diffraction Standards (JCPDS) using conventional methods An X-ray diffraction analysis was performed for CNTs. The samples were placed in a holder of Lucite and then on the goniometer of the diffractometer (Siemens D-5000 diffractometer with a copper anode X-ray tube with λ = 1.543 Å). *Ka* radiation was selected with a diffracted beam monochromator at 25 kV and 2θ steps of 0.02˚ for 50 min to acquire X-ray patterns from 4˚ to 70˚, with high enough intensities to achieve the lines to identify in angle 2θ the mineral components of the analysed material. Compounds were identified by comparing the diffraction patterns to the Joint Committee on Powder Diffraction Standards (JCPDS) using conventional methods [24].

2.2.3. Thermal Stability

5 mg of the samples were placed directly into platinum crucible, and the analysis was carried out under N_2 flow at the heating rate of 10˚C min^{-1}, with the temperature ranging from room temperature up to 950˚C using a TGA-TDA 51 TA Instruments Thermo gravimetric Analyser.

2.2.4. Specific Surface

Specific surface area (SSA, m^{2}g^{-1}) were determined for both dry and degassed

natural carbon nanotubes using a multipoint N_2 adsorption/desorption Brunauer-Emmett-Teller (BET) method at room temperature in a Micrometrics BEL Japan INC surface area analyser.

2.2.5. Raman Studies

Raman spectroscopy is one of the most powerful tools for characterization of CNTs. Without sample preparation, a fast and nondestructive analysis is possible. All allotropic forms of carbon are active in Raman spectroscopy [25], and the position, width, and relative intensity of bands are modified according to the carbon forms [26]. The Raman analysis was carried out using a Horiba JobinY-von spectrometer, HR Lab Ram 800. The laser was used to excite the sample, 532 nm. All the measurements were performed at room temperature.

2.3. Preparation of CNTs Filters

Removed system was built as presented in **Figure 1**, the filter was made of stainless steel with standard diameter of 0.05 m, inside it, on each side there was paper whatman No. 44 and 1 g of packed bed of CNTs. One of the most important features of this apparatus is its direct flow measurement and temperature of air pollutants before and after passing through the CNTs filter. The apparatus was put in exit tail pipe to obtain each component of gaseous emissions, the results of sorption experiments were obtained by gas analyser of one verificenter.

2.3.1. Interaction CNTs—Mobile Emissions

A study in 2009, realized by the Center for Sustainable Transport in Mexico, found that in the Toluca city, the car brands: Nissan-Tsuru 1997, 1999, 2008, Chevrolet-Chevy 1998, Chevrolet-Corsa 2007, have more presence and 87% of the vehicles are personal and private and four-fifths of them run every day. For this reason in it investigation, the vehicles were randomly selected and were used five cars of these brands. The experiments were carried out in the verificenter
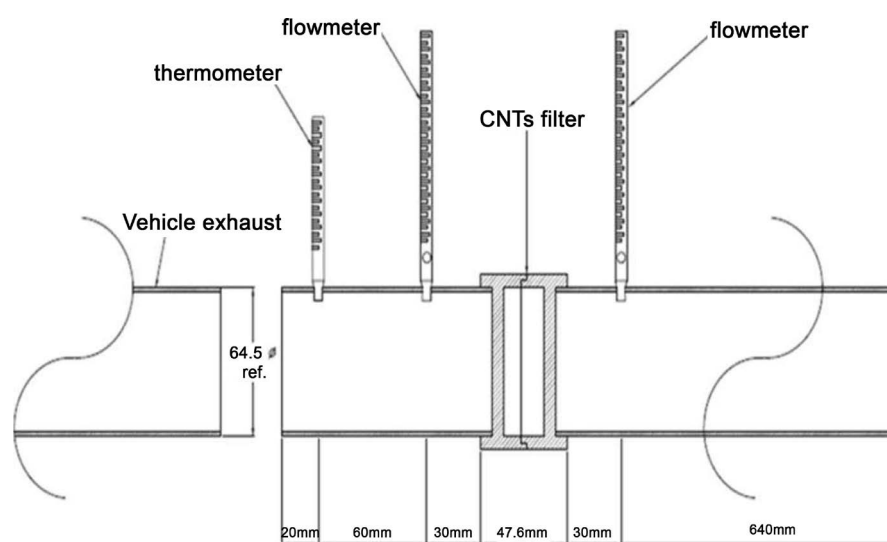

Figure 1. Experimental setup used for testing the removal efficiencies of CNTs filter.

TO-913 Macrover Auto SAQ. S.A. de C.V., located in Ignacio Comonfort Avenue, Santa Ana Tlapaltitlán, Toluca, México. The car emissions of hydrocarbons (HC), oxides of nitrogen (NO_x), carbon monoxide (CO) and carbon dioxide (CO_2), were verified according to program.

2.3.2. Removal Efficiencies of CNTs Filter

In this study, the concentrations of air pollutants after passing through the CNTs filter were calculated using the following equation [22]:

$$\text{Removal efficiency of CNT filter} = \left(1 - \frac{\text{Cwith-CNTs}}{\text{Cwithout-CNTs}} \times 100\%\right)$$

where $C_{\text{with-CNTs}}$ is the flow of air pollutants after passing through CNT filters, and $C_{\text{without-CNTs}}$ is the flow of air pollutants passing through membrane supports without CNTs loading.

3. Results and Discussion

3.1. Physicochemical Characterization of CNTs by Several Techniques

3.1.1. Morphology and Elemental Composition (SEM & TEM)

1) *Scanning Electron Microscopy before sorption process*

The carbon nanotubes analysed in this work were colour black. The SEM image 20,000 magnification for CNTs is shown in **Figure 2(a)**, in this can be observed that the bulk of the material is mainly constituted by fibbers; the material has a variety in diameter from 25 to 130 nm and 15 to 50 μm in length.
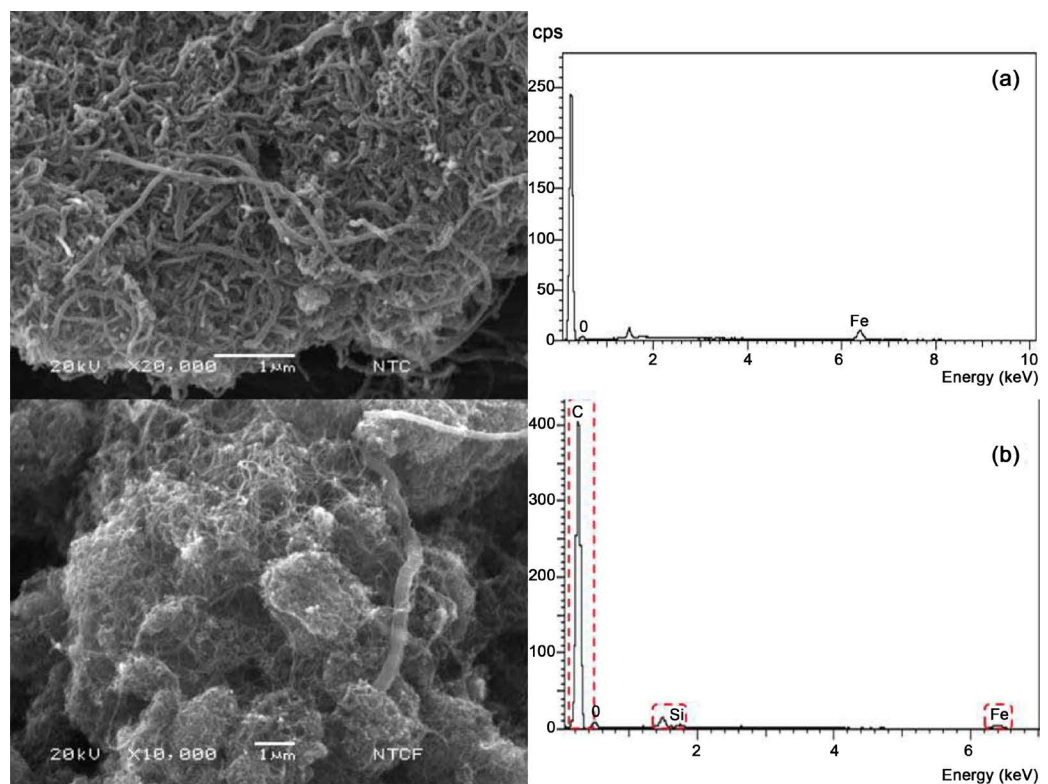

Figure 2. SEM image and EDS of carbon nanotubes (a) Before and (b) After sorption process.

In conjunction with electron microscopy, elemental chemical composition was determined. The identification of surface feature was performed by qualitative EDS analyses. The EDS results are: for the CNTSs were found: C (91.29%), O (6.23%) and Fe (2.48%). In this cases iron nanoparticles were used as the catalyst, for this the presence or iron in this percentage.

2) *Scanning Electron Microscopy after sorption process*

Below are the micrographs of the CNTS used in sorption of gaseous pollutant of exhaust from mobile sources, where it is observed that the morphology of the CNTS representative is unchanged, **Figure 2(b)**, also in chemical composition, where in the initial percentage of unchanged: 82.70% C, 15.66% O, 1.24% Fe, however was found the presence of silicon (Si), although at a low concentration of 0.38%.

3) *Transmission Electron Microscopy analysis*

These studies confirm the collected material consists of multi-walled carbon nanotubes (MWCNTs), with the dominant tube diameter in the range 72.5 nm with length 50 μm and the inter-tube spacing is of 0.34 nm, **Figure 3**.

3.1.2. X-Ray Diffraction (XRD)

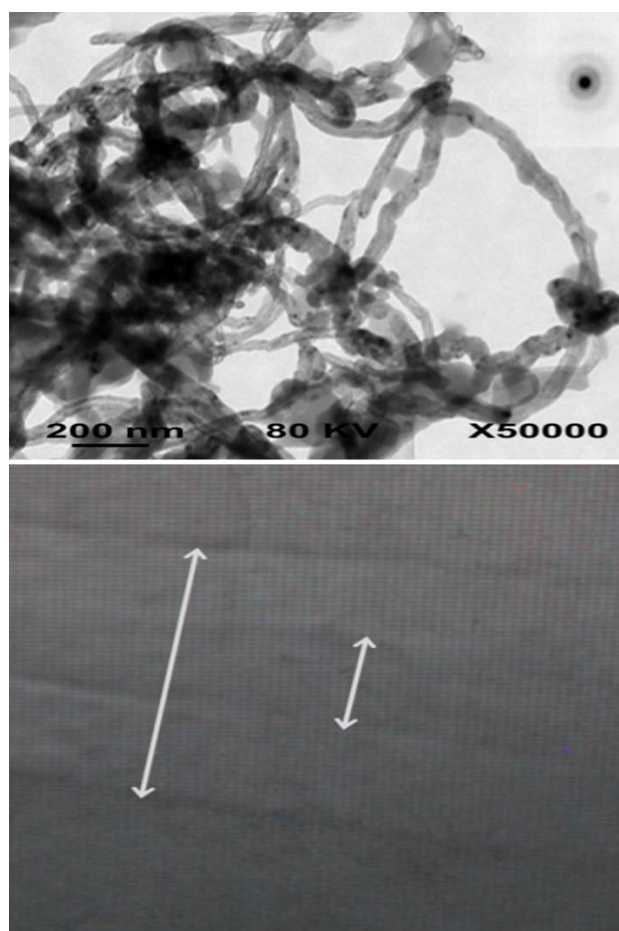According to the Joint Committee on Powder Diffraction Standard (JCPDS, card

Figure 3. TEM images of CNTs. Internal and external diameter range: 2 - 20 nm.
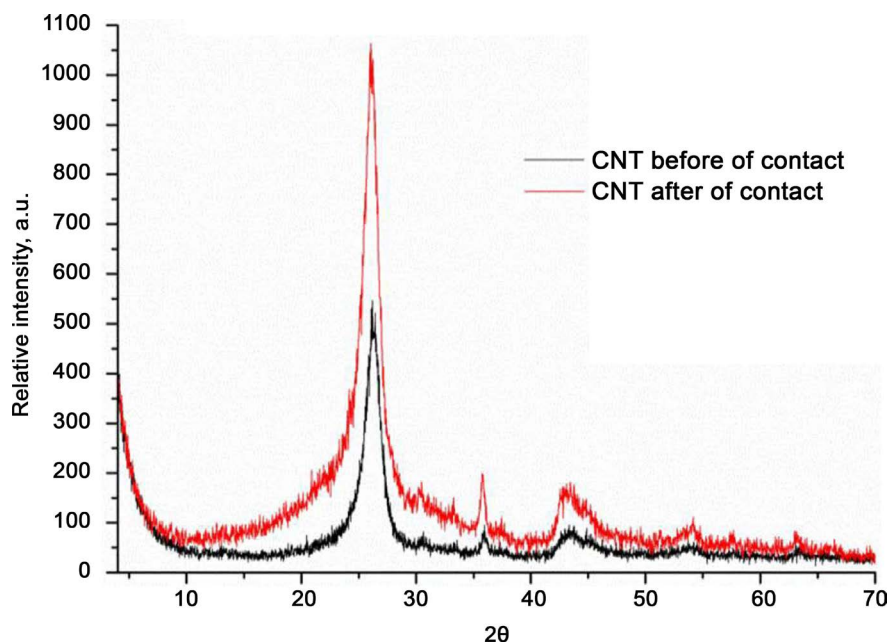
Figure 4. XRD patterns of CNTs before and after of contact with air pollutants.

01-075-2078), the main mineral compound present in CNTs is graphite. The intensity of the strongest peak to 26° for graphite is considered to represent the crystalline compound, and the intensity between 43° and 46° represents the background due to amorphous components. This behaviour indicates that the material does not suffer modification of its structure, **Figure 4**.

3.1.3. Thermal Stability
Thermal analysis methods are useful for identifying relative changes due to processing. It was used to study the degree of CNTs purification [25]. The loss of weight were from 25 to 800°C of 3.78%, from 800 to 870°C of 0.46%, from 870 to 900°C of 2.34% and 900 to 1000°C of 3.71%. In agreement to the results, it is confirmed that the CNTs do not present a high loss of weight (10.5%), **Figure 5**.

3.1.4. Specific Surface of Carbon Nanotubes
The total surface area (TSA) determined from classical BET method by physisorption of nitrogen at 78 K is presented. The CNTs showed that specific surface area is of 153 m^2/g, the total pore volume of 0.9534 cm^3 g^{-1} and an average pore diameter of 24.931 nm, classifying to the CNTs as mesoporous material (2 to 50 nm) according to the IUPAC classification. The data were analysed using the Langmuir adsorption model. It was concluded that CNTs had greater adsorption capacity, **Figure 6**.

3.1.5. Raman Spectroscopy Studies of Carbon Nanotubes
The Raman spectrum of CNTs sample is indicated in **Figure 7**. As shown, the band at 1580 cm^{-1} (G band) is due to tangential stretching of the carbon atoms in a two dimensional hexagonal lattice as a graphite sheet, this band reveals the presence of multi-walled nanotubes in the sample. The peak centered at around
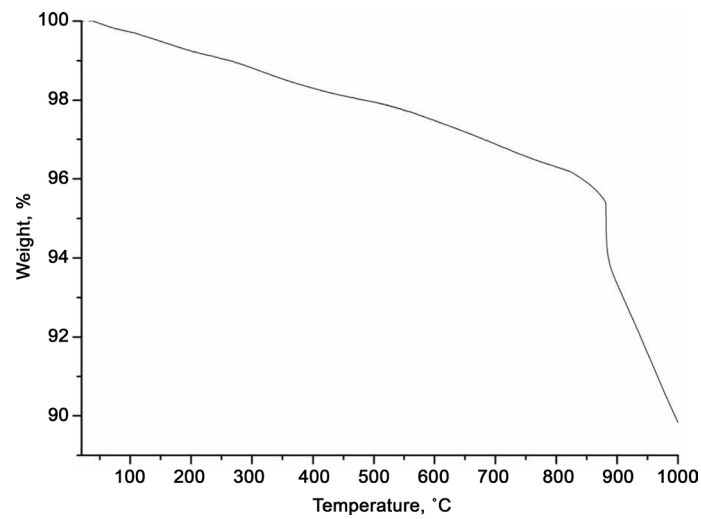
Figure 5. Thermogravimetric analysis (TGA) has demonstrated that nanotubes (CNTs) are stable.
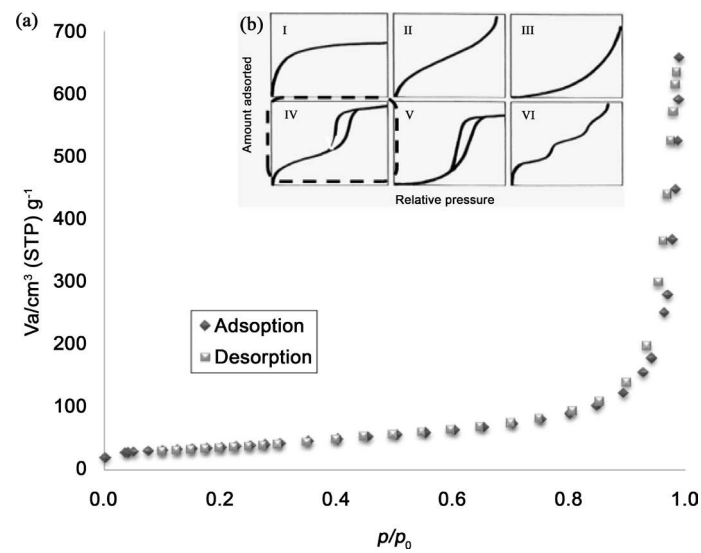

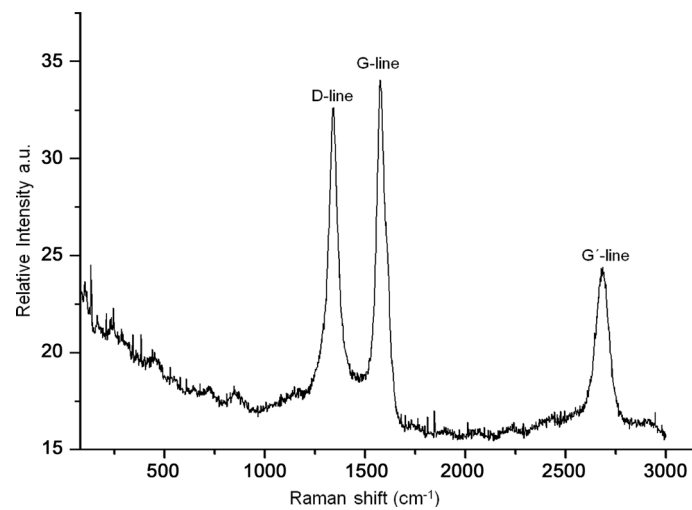**Figure 6.** Adsorption and desorption isotherms of CNTs.

Figure 7. Raman spectrum of carbon nanotubes.

1349 cm^{-1} (D-band) indicates disturbances on the hybridization of sp^2 carbon atoms and has its overtone at 2681 cm^{-1}, is mainly due to the presence of amorphous carbon and defects in the sample [27]. These two positions are close to 1346 cm^{-1} and 1578 cm^{-1} which have been reported in the literature as features for multi-walled nanotubes concentric hexagonal lattice [28].

3.2. Removal Efficiencies of CNT Filters

3.2.1. CNTs BET before Sorption Process

Table 1 and Table 2 show the vehicle models that were tested, presents the average removal efficiencies obtained, there can be seen that reduction of air pollutants using the sorption device packaged with the CNTS it is different for each vehicle.

For the tests conducted Corsa 2007, the flow was maintained at 80 mL/min, the temperature varied between 40°C and 50°C. For 1998 Chevy, the flow was 110 mL/min and the temperature at 70°C, to Nissan models 1997 and 1999, the flow varied between 85 and 90 mL/min, the temperature was 85°C, 2008 model presents a flow of 40 mL/min, and the temperature was 40°C.

The maximum permissible emission of pollutants applies to vehicles that are

Table 1. Comparison of average emission results.

Vehicle	Model Year	Gases		unfiltered	with filter	% Rem.
Corsa	2007	CO	% Vol	0.19	0.02	89
		HC	ppm	13	5	62
		CO_2	% Vol	15.90	15.80	0.6
		NO_x	ppm	335	16	89
Nissan Tsuru	1997	CO	% Vol	0.66	0.57	14
		HC	ppm	370.4	128	65
		CO_2	% Vol	11.52	11.06	4
		NO_x	ppm	108	83	23
Nissan Tsuru	1999	CO	% Vol	270	160	41
		HC	ppm	134	101	25
		CO_2	% Vol	14.19	10.06	29
		NO_x	ppm	468	6	57
Nissan Tsuru	2008	CO	% Vol	0.52	0.02	96
		HC	ppm	6	5	17
		CO_2	% Vol	11.71	8.9	24
		NO_x	ppm	19.2	5.6	70.8
Chevrolet Chevy	1998	CO	% Vol	3	0	100
		HC	ppm	2.4	0.02	99
		CO_2	% Vol	14.69	14.02	4.6
		NO_x	ppm	15	3	80

Table 2. Comparison of average emission results, fast idle.

Vehicle	Model Year	Gases		unfiltered	With filter	% Rem.
CORSA	2007	CO	% Vol	0.02	0.02	0
		HC	ppm	12	8	33
		CO_2	% Vol	16	15.80	1
		NO_x	ppm	180	19	89
Nissan Tsuru	1997	CO	% Vol	0.69	0.69	0
		HC	ppm	173.2	159.8	8
		CO_2	% Vol	11.96	11.89	0.6
		NO_x	ppm	99.6	30.4	70
Nissan Tsuru	1999	CO	% Vol	0.05	0.04	20
		HC	ppm	7	6.9	2
		CO_2	% Vol	12.4	9.7	22
		NO_x	ppm	456	110	76
Nissan Tsuru	2008	CO	% Vol	0.5	0.02	96
		HC	ppm	8	6.7	16
		CO_2	% Vol	16	11.02	31
		NO_x	ppm	19	17.7	7
Chevrolet Chevy	1998	CO	% Vol	0.7	0.44	37
		HC	ppm	128	115	10
		CO_2	% Vol	18.5	11	41
		NO_x	ppm	84	6	93

evaluated under this test, are given by the Mexican Official Standards NOM-041-SEMARNAT-1999 [29] and NOM-050-SEMARNAT-1993 [30] that apply to gasoline vehicles.

As shown in **Table 1**, the summary Comparison of Average Emission Results, was significantly higher variability was observed for the removal efficiency of the MWNT filters when collecting CO and NO_2. Nonetheless, the average removal efficiency of the CNT filters were observed for all air pollutants, but the removal efficiency was less. For the first test, the emissions were taken when vehicles were accelerated to 4 km/h.

Table 2 shows summary Comparison of Average Emission Results for the test fast idle (40 km/h) for different vehicles, shows the removal efficiencies of MWNT filters when collecting four air pollutants, CO, HC, CO_2, NO_x. However the removal efficiency for the CNT, was found significantly higher for NOx in all vehicles.

Nissan vehicles presented variability in its results; this is because they are different models. However the 2008 model had higher removal efficiency of the contaminants. The vehicle Corsa 2007 Chevy 1998 showed higher removal efficiency for NO_x.

3.2.2. CNTs BET after Sorption Process

After the removal, the CNTs showed that decrease 16% in BET surface area, it was 128 m^2 g^{-1}. The total pore volume of 0.9999 cm^3 g^{-1} and an average pore diameter of 31.06 nm, according to the IUPAC classification as mesoporous material (2 to 50 nm). The data were analysed using the Langmuir adsorption model. It was concluded that CNTs do not showed changes in adsorption capacity. Nitrogen adsorption isotherm of the CNTS, after sorption, follows the behavior of type IV and V of the physical adsorption isotherms IUPAC.

4. Conclusions

The CNTs were identified such as multi-called material and they were composed of carbon, 91.29% and oxygen, 6.23%. The characterization of these showed that the bulk is mainly constituted by fibbers. XRD confirm the presence of graphite. They are formed of two layers according Raman studies.

They have a specific surface area of 153 m^2/g classifying them as mesoporous material, but after removal gases, the specific surface area decreases to 128 m^2/g, showing that gases were sorbed. CNTs can be used to remove gases harmful to the health of mobile sources, but their efficiency depends of different variants.

Acknowledgements

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