Synthesis , morphological, structural and topological characteristics of carbon nanosphere derived from Iraqi diesel

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Abstract .The objective of this study involves the synthesis of carbon nanospheres(CNS) from incomplete burning of Iraqi diesel. Also, the synthesized CNS were further treated with hydrochloric acid and sonicated for 1 hour to achieve modified CNS. The results reveal that the produced carbon nanoparticles much smaller than those from the conventional diesel combustion. CNS were characterized using FT-IR spectroscopy (FTIR), scanning electron microscopy(SEM), atomic force microscopy(AFM), X-rays diffraction(XRD), Energy dispersive x-ray microanalysis (EDX), Brunauer-Emmett-Teller (BET) and Thermo gravimetric analysis (TGA). FTIR spectra showed a change in nature of functional groups and exiting of adsorbed impurities on surface of synthesized carbonic materials. The results obtained from of SEM and XRD show a similar structure and morphology of the new materials. Thermal gravimetric analysis (TGA) analyses indicate a gradual weight loss in the temperature range from 0°C to about 700°C. AFM and BET analysis indicted a similar topology and surface area values of both materials. EDS analysis exhibited that carbon was the main product of diesel combustion.

Keywords: diesel, carbon nanospheres, SEM, BET, XRD.

Introduction

The diesel considered as a main source of energy for many aspects of contemporary life, where it plays a vital role in the field of power generation in many applications such as commercial transport, trucks, buses, agricultural equipment, ships, and power Stations. It's also being used for construction and industrial activities (1-4).

Recent observations have indicated that diesel may provide other benefits with regard to particulate emissions, because of the incomplete combustion of diesel fuel in high temperature environments, soot is produced (5,6). Diesel fuel has a significant impact on the character and properties of soot produced from it, therefore on the soot reactivity, where physical and chemical properties of emitted soot particles are influenced from combustion of diesel (7). Even though the presence of soot is long known, the complex formation pathway for it is still under investigation. Structural changes in the composition of soot suggest a changes in the interactions of its nature. The soot aggregate morphology is of great
importance point in experimental side, where experimental observations suggest that aggregate and particle size distributions should be taken into account to correctly model soot properties. Many studies reported a variety of techniques that have been employed to synthesize of carbon nanoparticles from diesel and other carbonic sources. But the mechanism of soot formation stays not completely understood and the mechanisms responsible for soot formation remain unclear.

In the recent past years, the advances in analytical equipment in laboratory resulted in the ability to undertake more important study of a wide range of substances generated from the combustion of hydrocarbons. Therefore, it is necessary to search for cheap sources and simple techniques for preparation carbon nanomaterial. In this paper, a simplified method of economic production of carbon nanoparticles was adopted using diesel oil as raw material.

Experimental Part

Chemicals

The diesel used in this study was obtained from the Company of South Refineries Company and used without further purification. Ethanol (Scharlau 99.9%), Acetone (Scharlau 99%), Hydrogen peroxide (Sigma 30%), Hydrochloric acid (Scharlau 37%), were used without further purification.

Instruments

IR Spectra were recorded using Shimadzu FT.IR8000 Series (Shimadzu). SEM images were recorded using TESCAN VEGA3. Energy dispersive x-ray microanalysis (EDX) attached to the SEM was employed to measure the elemental analysis. Thermo gravimetric analysis TGA was performed using LINSEIS-STA PT-1000. Labtcc-410 sonication bath was used for dispersion of prepared materials. XRD Pattern was recorded using XRD-600. Triumph Ultracentrifuge was used for separation of soot. AFM image was acquired with AA2000 atomic force microscopy (Angstrom advanced Inc.). The Brunauer-Emmett-Teller (BET) surface areas were measured from the N₂ adsorption using a Quadrasorb SIMP. Barretl –Joyner-Helenda(BJH) method equation was obtained to measure of pore size.

Synthesis of Carbon nanospheres

Diesel was placed into simple laboratory lamp with a combustible cotton material, then the cotton material were saturated with diesel overnight. The lamp lit is allowed to burn and a clean pyrex beaker was placed above the lamp to collect soot emitted from it. The process continued until collection approximately 10 g. The black material was washed using organic solvents (ethanol, acetone) several times to remove unburned fuel. Then it converted to suspension in ethanol and sonicated for 1 hour, then it separated by ultracentrifuge (10000 rpm) and dried in an oven at 100 °C for 4 hours. Then, 5 g of produced soot was suspended and stirred in 100 mL of 0.1 N hydrochloric acid for two hours. The treated carbonic material was separated and washed several times with acetone and ethanol to remove traces ions. Then it was sonicated for 1 hour, and separated using ultracentrifuge at 10000 rpm and dried in oven at an 100 °C for 4 hours.

The carbonic materials are donated as CS1: pristine soot, CS2: treated with HCl.

Results and Discussion
In this research, diesel has been used as a carbon source for production of carbon soot. Carbon soot was produce by combustion decomposition of diesel oil, which performed by the breakup of long petroleum series to shorter ones. Then, the collected carbon soot has been retreated with hydrochloric acid.

The morphological, thermal, topological and structural properties of carbon soot were investigated by Fourier transform infrared FTIR, scanning electron microscope SEM, energy-dispersive X-ray EDX, X-ray diffraction spectroscopy XRD, Thermo gravimetric analysis TGA and Atomic force microscopy AFM. Brunauer-Emmett-Teller (BET) and Barret–Joyner-Helenda (BJH) methods were employed to evaluation of surface area and pore size respectively.

**FTIR analysis**

FTIR spectroscopic analysis was carried out to investigate the presence of the functional group in CNS and treated CNS. Thermal decomposition of diesel produces mainly carbon soot that has elemental carbon and carbonic material with low hydrogen content, it also may contain hydrocarbon residue. Figure 1 illustrates the FTIR spectra of CNSs. The spectra indicated the presences of functional groups of hydrocarbon. Weak peaks between 3650-3800 cm\(^{-1}\) are belong to O-H stretch, peaks 3425 and 3415 cm\(^{-1}\) is attributed to N-H vibrations. The peaks at 2425 and 2415 cm\(^{-1}\) are assigned as C-H stretching vibrations at 1620, 1558, 1515 cm\(^{-1}\) are assigned as aromatic rings. A very weak peak at 1334-455 and 1319-401 cm\(^{-1}\) is for C-H stretching, vibration\(^{(22-24)}\).

**Figure 1:** FTIR spectra for CS1 (a) and CS2 (b).
SEM Analysis

A typical SEM image of synthesized carbonic materials is presented in Figure 2. The images are clearly show the spherical and semispherical particles irregular shaped nano-particles forms. The SEM micrographs of carbonic materials were performed to study the characteristics of surface morphology. These particles join together to form chains of spheres. The synthesized nanoparticles have a size range as shown in Table 1. It is clear that most carbonic particles are in a size range below 100 nm and at diameter average about 70 nm \(^{(25,26)}\).

Table 1: Morphological characteristics for carbon nanomaterial

| Material | Diameter range, nm | Diameter average, nm | Particles shape         |
|----------|--------------------|----------------------|-------------------------|
| CS1      | 52-83              | 60                   | Spherical, semispherical|
| CS2      | 55-87              | 70                   | Spherical, semispherical|

Figure 2: SEM images for CS1 (a), CS2 (b).
EDX analysis

Energy disperse spectroscopy (EDX) technique was employed to study the purity and elemental analysis of synthesized CNSs. EDX spectra are shown in Figure 3, which indicates the presence of carbon as a main combustion product of diesel. Also, CNSs composites include detectable limits of oxygen, chloride and sulphur. The combustion of diesel indicates the product to consist of about 93.4% carbon (CS1) which slightly increases to 96.3% under treatment of CNS with hydrochloric acid (CS2). As the results shown, the low impurities ration indicating the production of acceptable purity materials.

Figure 3: EDS analysis for CS1 (a), CS2 (b).
TGA analysis

Thermal gravimetric analysis (TGA) was employed to investigate the thermal stability of the synthesized CNSs. TGA curves of soot materials are presented in Figure 4. The obtained thermal gravimetric curves indicate a gradual weight loss in the temperature range from 0°C to about 650°C. In both soot materials, a weight loss of not exceed 47% only of initial weight in the above temperature range. The weight loss started from 141.80 to 643.8 °C indicating decomposition of diesel and forming carbonaceous material. (27,28)

Figure 4: TGA analysis for CS1 (a), CS2 (b).

XRD Analysis:

The XRD analysis was adopted to investigation the crystal structure of synthesized nanomaterials. Figure 5 shows the XRD patterns of synthesized carbon nanospheres. The XRD patterns show presence of two Bragg diffraction peaks at 2θ = 11.30°, 24.15° and 42.23° for CS1 and at 2θ = 11.52°, 24.15° and 42.23° for CS2.
and $23.91^\circ$ or CS2. The two intensively correspond to hexagonal graphite lattice and indicate the presence of amorphous carbon\textsuperscript{15,29}.

![XRD patterns for CS1 (a), CS2 (b).](image)

**Figure 5**: XRD patterns for CS1 (a), CS2 (b).

**BET Analysis**

Spesific surface area of carbon nanospheres was calculated using Brunauer-Emmet-Teller (BET) method. Pore size distribution of both materials was obtained from Barret -Joyner-Helenda(BJH) method equation using adsorption isotherm. Figure 6 presents the nitrogen adsorption/desorption isotherm and pore size distribution of carbon materials. The results indicate a slight increase of both specific surface area and mean pore sized in CS2 material. Also, as figure 6 recles, the carbonaceous materials show typical IV isotherms. Table 2 showed that the value of the pore diameter exhibited that CNSs synthesized in the present work are mesoporous materials\textsuperscript{(30)}.

| Material | Specific surface area, m$^2$/g | Mean pore diameter, nm | Total pore volume, cm$^3$/g |
|----------|-------------------------------|------------------------|----------------------------|
| CS1      | 65.045                        | 45.47                  | 0.738                      |
| CS2      | 69.972                        | 48.20                  | 0.843                      |

Table 2: Surface areas and pore size for CNSs
AFM Analysis

Surface topology and thickness of synthesized materials were analyzed by employing atomic force microscopy technique. Figure 7 shows the D2, D3 images and granularly cumulative distribution of CNSs. Table 3 summarizes the surface roughness coefficient (Sa), thickness, root mean squared (Sq), surface skewness (Ssk), surface kurtosis (Sku), and average diameter values. As results clarify, the treated of CNS with hydrochloric acid increases the surface roughness coefficient and decreases the average diameter, but in same time it slightly increases the thickness.

Table 3: Statistical values for CNSs

| Amplitude factor | CS1   | CS2   |
|------------------|-------|-------|
| Sa               | 0.681 | 1.26  |
| Sq               | 0.796 | 1.53  |
| Ssk              | -0.262| -0.289|
| Sku              | 1.95  | 2.46  |
| Thickness        | 5.00  | 7.81  |
| Average diameter | 95.08 | 88.24 |
Figure 7: D2, D3 images and granually cumlatives distribution for CS1(a) and CS2(b).

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