This study reports on the crude oil-sensing using carbon nano structures (CNSs). A mixture of CNSs was obtained by a simple method of preparation using palm cellulose ash and nitric acid as precursors, the powder was characterized by x-ray diffraction and infrared spectroscopy. The optical density of crude oil from Rhoud El-Baguel area (Southeast of Algeria) studied using UV-Vis spectroscopy, before and after adding an amount of CNSs powder to view the CNSs crude oil sensing and therefore a new method to determine the quality of crude oils and the comparison between them. Results show that CNSs prepared from palm cellulose ash have a good crystallinity and it is formed mainly from carbon nano dots (CNDs) with 4.32 Å in layers spacing and 7.4 Å in crystallite size, indicate that CNSs can be used as an excellent crude oil sensor.

In the petrochemical industry, knowledge of the quality and content of crude oil is a key factor in improving the refining process. Methods of spectroscopy are the most important methods used because they contain important informations regarding the chemical properties of each sample. The compounds in oil, responsible on optical response named: Fluorophores (Table 1), which are compounds that absorbs in the UV-visible range. This condition is fulfilled for conjugated electron systems, such as polyunsaturated molecules and aromatics.

Nano carbon structures have a wide range of interest because of their use in applications such as energy storage, tribology, electronics, medicine, catalysis and sensors. Carbon nano structures (CNSs) are an ultra-small photoluminescent (PL) nanomaterial (<10 nm), It has significant optical properties, disposable surface functions, chemical inactivity, high photosensitivity, simple and inexpensive methods of preparation, and an abundance of raw materials... CNSs are crystals which can act as a sensor by sparkling at the desired wavelength or color. We emphasize that fluorescent organic molecules are often aromatic or contain multiple bonds, which are alternating single and double bonds, responsible for the high-octane number and therefore the quality of petroleum.

**Experimental and Methods**

**Extraction of Cellulose from Phoenix Dactylifera L. tree.** The Phoenix Dactylifera L. leaves were crushed and screened to ensure that the particle size was distributed from 8 meshes to 30 meshes. Leaves were immersed in 5 wt% sodium hydroxide solution at ambient temperature for 12 h. Then they were washed with water for several times and dried in the oven at 80 °C for 24 h. To remove the wax, the debris of leaves were immersed in the solution of methylbenzene and ethyl alcohol (volume ratio of 1:1), and kept boiled for 8 h. The residues were washed with ethyl alcohol several times and then dried in the oven at 80 °C for 24 hours. And to remove lignin, leaves were soaked in hydrogen peroxide (30 vol%) and acetic acid solution (volume ratio of 1:1), and boiled with magnetic stirring at 60 °C for 7 h. Water was used to wash the residue and then filtered until the filter was neutral. The fibers obtained were boiled in 5 wt% of sodium hydroxide solution at 80 °C for 2 h, then,
| Fluorophore       | Chemical structure | Fluorophore       | Chemical structure |
|-------------------|--------------------|-------------------|--------------------|
| Benzene           | ![Benzene](image)  | Phenol            | ![Phenol](image)   |
| p-cresol          | ![p-cresol](image) | dibenzofuran      | ![dibenzofuran](image) |
| Acenaphthene      | ![Acenaphthene](image) | Carbazole        | ![Carbazole](image) |
| Chrysene          | ![Chrysene](image) | Benzo(a)pyrene   | ![Benzo(a)pyrene](image) |
| p-methylanisole   | ![p-methylanisole](image) | dibenzothiophene | ![dibenzothiophene](image) |
| Phenanthrene      | ![Phenanthrene](image) | Pyrene           | ![Pyrene](image)    |
| Porphyrin         | ![Porphyrin](image) | Toluene          | ![Toluene](image)   |
| m-Xylene          | ![m-Xylene](image) | Indole           | ![Indole](image)    |
| Naphthalene       | ![Naphthalene](image) | 2-Naphthol       | ![2-Naphthol](image) |
| 2,3-Benzofluorene | ![2,3-Benzofluorene](image) | Anthracene      | ![Anthracene](image) |
|                    |                    |                   |                    |
| Continued          |                    |                   |                    |
washed with water to neutral and dried in the oven at 80 °C for 24 h. The cellulose fibers from Phoenix Dactylifera L. leaves were obtained.\textsuperscript{12,13} 

**Synthesis of carbon nanostructures (CNSs).** In order to obtain C-nanostructures, the cellulose extracted previously was carbonized in a muffle furnace directly at 240 °C for 2 h.\textsuperscript{4} About 5 g of fine ashes obtained from cellulose furnace and mixed with concentrated nitric acid (60%) and stay in agitation for 24 hours. The mixture was separated by centrifugation at 12,000 rpm for an hour to separate the residue and supernatant. The latter was heated in a vacuum oven at 200 °C.\textsuperscript{14}

**Crude oil optic sensing.** The oils were excited by ultraviolet rays (300–400 nm) which fluoresce in the visible wavelength range of 400 to 600 nm. The crude oil sample was obtained from Rhoud El-Baguel, close Hassi-Messaoud region, city of Ouargla south eastern of Algeria. To perform optical density measurements, it was required to dilute the sample to obtain a transparent solution to transmit the light. Cyclohexane was chosen as solvent that can optically respond in the range of 350 nm–500 nm, wavelengths used to excite crude oil.\textsuperscript{15,16} Six samples of oil diluted in cyclohexane at different concentrations were used for the measurements. Table 2 shows the different concentrations of prepared samples. Absorption spectra of all samples were measured at room temperature. at 350, 400,450 and 500 nm.

**Characterization of carbon nanostructures (CNSs) and optic sensing.** The type of the carbon Nano structure was analyzed by X-ray powder diffraction (XRD) using a BENCHTOP PROTO AXRD diffractometer in the range 2θ:10–80°(step: 0.1°) and CuKα1 Source (λ = 1,54 Å). Fourier transform infrared spectra were obtained on a SHIMADZU 8400 s (FT-IR) spectrometer whose extent is between 400 and 4000 cm\(^{-1}\). UV/visible absorption spectra were recorded with a UV/VIS 6305 spectrophotometer (JENWAY Company).

Table 1. Some Fluorophore found in crude oil.\textsuperscript{26}

| Fluorophore | Chemical structure |
|-------------|-------------------|
| Perylene    | ![Perylene](Image) |

Table 2. Concentration of oil in cyclohexane.

| Sample | Concentration (ml/l) |
|--------|----------------------|
| 1      | 0.5                  |
| 2      | 1                    |
| 3      | 1.5                  |
| 4      | 2                    |
| 5      | 2.5                  |
| 6      | 3                    |

Figure 1. Powder XRD of carbon nano structures sample.
Results and Discussion

Characterization of CNSs by XRD. Figure 1 shows the X-ray diffraction pattern of Carbon-Nanostructures (CNSs) produced by one-step thermal carbonization. For carbon nanodots (CNDs), a non-relief reflection band centered on $2\theta = 21.68^\circ$ corresponds the (002) lattice spacing of carbon-based materials with amorphous nature or shows a shift down; what is indicates an increase in sp$^2$ layer spacing.

Crystal planes and a small broad peak to about $2\theta = 44.22^\circ$ and $77.5^\circ$ correspond to the set (100) and (110) reflections. The spacing between the layers was calculated by applying the Bragg equation and found at approximately 4.23 Å. As long as the average crystallite size, $L_c$, can be determined using the Scherrer equation:

$$L_c = \frac{K\lambda}{\beta \cos \theta}$$

or:
- $\lambda$: the wavelength of X-rays (1.54 Å),
- $\beta$: the width at half height (in radians),
- $\theta$: the diffusion angle
- and $K$ is the Scherrer constant (0.9).

The $L_c$ has been estimated at 7.0 Å.

Infrared spectroscopy FTIR. As shown in Fig. 2, the existence of carbonyl (C=O) causes the peak of about 1696 cm$^{-1}$. The presence of oxygen-containing carbon structures has been confirmed. The peak at 1528 cm$^{-1}$ can be attributed to the C–C stretching vibrations. The $\delta$ (C=O) vibration band is found at approximately 680 cm$^{-1}$. The bands at 1900, 2098.172 and 2334.892 cm$^{-1}$ can been attributed to inorganic $\nu_3$CO$_3$, manganese carbonyl stretching frequency and water molecule under strongly hydrogen-bonded conditions.

In Fig. 3a it is possible to observe Rhoud El-baguel crude oil optical properties. It appears that the crude concentration varies proportionally with the optical density (OD) in all the domain of UV-Vis. After adding nano carbon, the concentration 0.4 ml/l shows the best OD (Fig. 3b) throughout the UV-Vis range.

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Figure 1. X-ray diffraction pattern of Carbon-Nanostructures produced by one-step thermal carbonization.

Figure 2. FT IR of CNSs Sample.

Figure 3. Effect of crude oil sample concentration on optical density at different light wavelengths: (a) before and (b) after adding CNSs powder.
The analysis also shows that the samples have a better optical density for a minimum value of wavelength (350 nm) and this for concentrations less than or equal to 0.4 ml/l. While it is less intense for other wavelengths throughout the UV-Vis domain (Fig. 4a). For comparison, the OD increases perfectly according to each concentration and in the whole area at 400 nm (Fig. 4b).

Figure 4. Effect of light wavelengths on optical density of crude oil sample at different concentration: (a) before and (b) after adding CNSs powder.

Figure 5. Optical density variation of different oil concentrations at 400 nm before and after adding CNSs powder.

Figure 6. Optical density variation of 0.4 ml/l oil sample at under different light wavelengths before and after adding CNSs powder.
In order to determine clearly the effect of carbon nanostructures on the optical properties of the oil sample, we study the optical density changes in terms of concentration of samples under a constant wave length of 400 nm before and after adding an amount of CNSs powder (Fig. 5). And we study the optical density changes in terms of UV-Vis wavelengths for 0.4 ml/l concentration of sample before and after adding an amount of CNSs powder (Fig. 6). It is clear that the optical density increases strongly by adding nanocarbon.

**Conclusion**

Carbon Nanostructures (CNSs) can be synthesized simply with an ash of palm cellulose available locally and maybe used as a very effective tool for sensing and estimating the quality of crude oil and comparing between them.

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Competing interests
The authors declare no competing interests.

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