



Carbone nanospheres synthesis by pyrolysis of crude oil and optimization of parameters growth by response surface methodology (RSM)

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ABSTRACT

Algerian oil as a new source of carbon is used to prepare the carbon nanospheres (CNSs) by pyrolysis method. A mixture of crude oil and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution as catalyst was injected into the reaction furnace to produce CNSs in an inert atmosphere, followed by multi step purification to remove different impurities. The carbon nanospheres have been characterized by scanning electron microscopy (SEM), energy dispersive X-rays spectroscopy (EDAX), X-ray diffraction (XRD), Raman spectroscopy and FTIR spectrum. The SEM image reveals that these CNSs have smooth surfaces and uniform particles with a diameter lower than 500 nm. the XRD and Raman studies shows that the graphitization degree of CNSs is not high, while the EDAX analysis shows that more than 98% of the CNSs is carbon. FTIR proved the presence of new functions after samples treatment such as acid function. This study reports the optimization of various process parameters such as, temperature of reaction ($860\text{-}940^\circ\text{C}$), process Time ($90\text{-}150\text{min}$) and mass ratio catalyst/Crude oil ($0.83 \cdot 10^{-3}\text{-}2.48 \cdot 10^{-3} \text{ g/g}$) for increasing the Yield of CNSs. A MODDE 6.0 experimental design was employed for the optimization of synthesis of crude oil to ensure high production of carbon nanospheres in a low catalyst concentration and high temperature for a short length of time. The analysis of variance showed a high coefficient of determination value ($R^2 = 0.965$) and Maximum CNSs production was predicted and experimentally validated, the optimized process conditions were identified to be reaction temperature of 900°C , duration synthesis of 113min and mass ratio catalyst /crude oil of $0.8 \cdot 10^{-3} \text{ g/g}$ with a yield of 13.23%.

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Introduction

In recent years, carbon materials have attracted considerable attention because of their novel morphologies and specially physical and chemical properties, such as fullerenes[1], nanospheres[2], nanotubes[3], onions[4], nanorods and nanocoils[5].

Among the various forms of carbon, carbon nanospheres as a new material is becoming increasingly important [6], due to their uniformity, high thermal stability, an excellent electrical conductivity[7], high surface area, high mechanical strength [8]. Furthermore, their intrinsic properties can be controlled easily by changing the production condition [9] or modifying the surface of the carbon sphere [10]. Owing to these merits, the carbon spheres have encountered interesting application in many fields such as in energy storage systems, as specific adsorption capacity of gases, polymer additives and electrochemical applications [11] as catalyst support [12], They can be used in secondary lithium ion batteries [13], lubricants[14], and as precursors for diamond film synthesis [15], and so on.

CNSs are synthesized using procedures similar to those that generate CNTs and CNFs. Thus, CNSs can be synthesized using arc discharge, laser ablation and plasma processes, shock compression techniques, chemical vapor deposition (catalytic and non-catalytic), autoclave processes (catalytic and non-catalytic)[16]. Hydrothermal treatment [17] with various carbon sources derived from synthetic and natural products have been used such as hydrocarbons (saturated, unsaturated, substituted,

etc.), polymers (polyethylene, polypropylene, etc.) and natural products (oils, plant fibers, etc.) [18].

In this work, we report a novel example of the formation of carbon nanospheres using crude oil as a carbon source; however, our survey of available literature indicates that crude oil has not been used as carbon precursor for the synthesis of carbon nanomaterial. Then the use of available material such as crude oil in production of carbon nanomaterial will have its economic reflection. During this work and for the first time, carbon nanospheres were synthesized utilizing Algerian crude oil by pyrolysis methods and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst under atmospheric pressure. Several experiments were conducted by pyrolysis; using different reaction conditions in order to optimize the synthesis parameters by MODDE6.0 Software using RSM model experimental Design. The variation of growth parameters was done systematically to investigate the effects of parameters such as process temperature, mass ratio (catalyst /crude oil) and reaction time to have a high Yield of CNSs.

Response surface modeling (RSM) model is preferred as design model since relatively few combinations of the variables are adequate to estimate potentially complex response function. It involves the process of planning of experiments, so that the appropriate data may be collected, analyzed and interpreted, resulting in valid and objective conclusions. In a statistically designed experiment, we simultaneously vary the factors involved in an experiment at their respective levels so that a

large amount of information can be gained with minimum number of experimental trails.

Experimental

Chemicals

Crude oil ($d=0.84$, $M_m=239\text{g/mol}$) is supplied by refinery of Adrar (Algeria), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ used as catalyst and a mixture HCl (35%)/ethanol utilized for preparing solution of catalyst, inert gas (Argon), the products such as Benzene, nitric acid HNO_3 (65% purity), chloridric acid HCl (37% purity) were used for treatments of CNSs, distilled water,

Carbon nanospheres production

In this study, CNSs were prepared from crude oil pyrolysis under atmospheric pressure in the presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The mixture: crude oil-catalyst solution with different ratios (Fe:C) were injected into a quartz tube ($L=70\text{cm}$, $d=27\text{mm}$) through a capillary and heated up to a certain temperature (750, 800, 850, 900, 950°C) using Argon as carrier gas and maintained for different times (60, 90, 120, 150, 180mn) (see fig.1). The quantity of crude oil injected in each run was 40 ml.

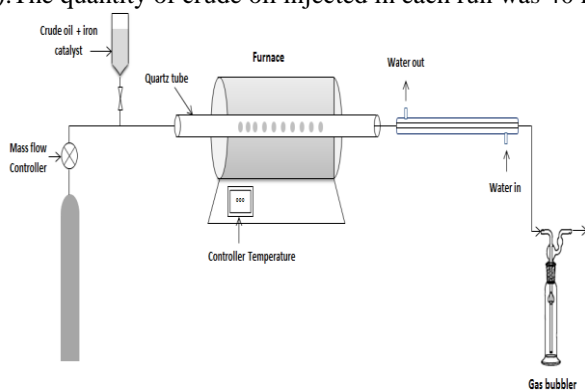


Fig 1. Schematic of the chemical vapor deposition equipment

After the reaction, the oven subjected to a cooling to room temperature. The black material formed on the inner wall of the quartz tube is recovered, milled and purified.

Purification of CNSs

The complete purification protocol is a two-step process. The first one consists in the removal of polyaromatics and soluble impurities; the second one is an acid treatment (HNO_3/HCl) to eliminate the metallic particles. A schematic representation of this procedure showed in fig.2. The detailed processes are as follows.

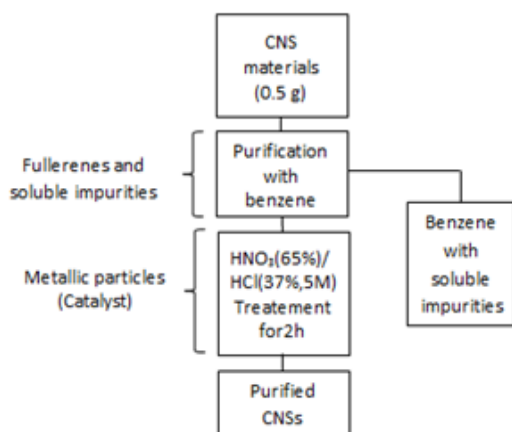


Fig 2. Step purification of CNS

Purification with benzene

The as prepared material (CNS) was treated and washed by benzene, and then filtered on the filter paper ($0.2\ \mu\text{m}$), the solid sample was dried in air at room temperature, the benzene used

in the purification was submitted to distillation, the resinous materials were dried.

Acid treatment with an HNO_3/HCl mixture

500 mg of the solid sample must refluxed for 2 h in 100 ml of (HNO_3/HCl) at 115°C . When the solution cooled down to ambient, CSs are filtered and washed with distilled water.

RSM and Variables Optimization

In the present study, RSM was used in the empirical study of the relationship between the measured responses and a number of input variables with the aim of optimizing response. Percentage of CSs synthesized is the response of the system while the three process parameters, temperature [$860\text{-}940^\circ\text{C}$], reaction Time [90-150 min] and mass ratio catalyst [$0.83 \cdot 10^{-3}$ - $2.48 \cdot 10^{-3}\ \text{g/g}$] were independent variables. The experimental cycle consists of three phases: 1) the design phase where we define our factors and within which ranges they must be varied, our response, objective, design and model.

2) The analysis phase where we explore our data, review the raw data and the fit, review diagnostics in plots and lists, refine and interpret the model.

3) The prediction phase where we use the model to predict the optimum area for operability.

The three levels and three-process variables viz., process temperature, time of reaction and mass ratio (catalyst/crude oil) are represented by X_1 , X_2 and X_3 respectively, the upper and lower limits of the process variables are shown in Table 1. A total of 17 experimental runs are necessary for a 2^3 full factorial design which consists of 8 factor points, 6 pivot points with three replications at center point, the number of experiments was calculated based on the formula [19] below:

$$N = 2^n + 2n + n_c$$

Where n is the number of factors; n_c is the center point of repeat runs. The correlation model of each of response value and experimental factors of X_1 , X_2 and X_3 were derived using a quadratic polynomial, as typically shown in Eq.1 [20]:

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j$$

Where, Y is the percentage of CNSs synthesis, b_0 the offset term, b_i the first orders main effect, b_{ii} the second order main effect and b_{ij} the interaction effect, X_i and X_j are experimental factor codes.

Characterization Techniques

The as prepared products were characterized by X-ray diffraction (XRD) performed on PANalytical X-ray diffractometer at CETIM - Boumerdes.

The surface morphology of the samples was examined with scanning electron microscopy (SEM) using a Scanning Electron Microscope FEI QUANTA 600W were used in order to check purity, phase's structure, surface morphology of the products.

Parameters used are accelerating voltage 5kEv, high vacuum, ETD detector, Working Distance 10mm.

Raman scattering measurements were recorded at room temperature using Horiba HR800UV. The samples were scanned between $100\text{-}4000\ \text{cm}^{-1}$. For all the spectra, a linear baseline correction was used and the peak analysis was performed with Origin lab- 8.0 software

The FTIR spectra of the carbon samples recorded over the range $4000\text{-}500\ \text{cm}^{-1}$ on Bruker spectrometer using the KBr pellet technique.

Results and Discussion

Algerian crude oil has been adapted as a new carbon precursor to prepare CNS under mild conditions, to our knowledge, which has never reported in the literature. After heated, crude oil decompose, resulting in a large amount of small molecules and carbonaceous species. The preliminary

results presented here lead one to believe that crude oil is another ideal main source for making carbon nanoparticles.

Scanning electron microscopy (SEM)

The SEM image of the CNSs shown in fig.3, Aggregates of carbon structures with globular morphology were observed from this image. The diameters of particles is lower than 500nm, as can be seen from Fig.3, the products consisted mainly of homogeneous carbon spheres appeared condensed and their surfaces are very smooth,

Fig.3a shows the SEM image of typical morphology of the carbon clusters consisting of carbon nanospheres directly after removal from the interior surface of quartz tube. While Fig.3b shows carbon nanospheres with a spherical shape obtained after treatments. The particles seem to be agglomerated with each other as a sphere form without impurities. No other structure such as carbon nanotubes or fibers is detected.

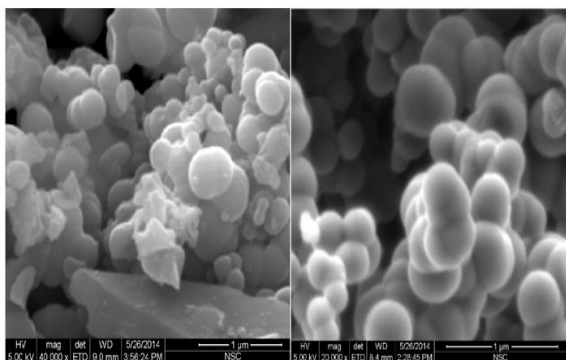


Fig 3. Scanning electron microscopy (SEM) images of carbon nanospheres produced by the pyrolysis of crude oil.

This result was confirmed by chemical analysis of product using EDX as in fig.4, also confirms the high yield of carbon (98.1%) after pyrolysis of crude oil at 900°C, the impurity element in this carbonaceous spheres is oxygen (1.9%).

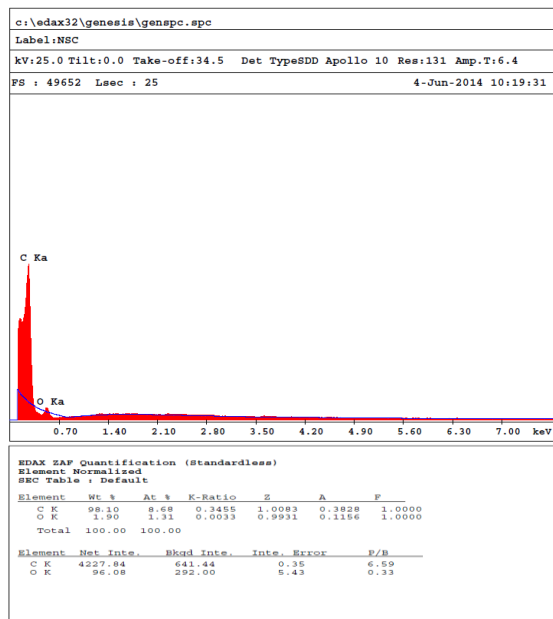


Fig 4. Dispersive energy of X-rays spectroscopy (EDAX) Raman Spectroscopy

Raman spectra can be used to characterize the graphitization of CNSs. The Raman spectra of the CNSs samples are shown in Fig.6, in which a strong peak around 1588.6 cm⁻¹ and a relative weak peak at 1343 cm⁻¹ can be clearly seen.

The peak at 1588.6 cm⁻¹ (G band) is attributed to the stretching modes of C-C bonds of typical graphite, while the peak at 1343 cm⁻¹ (D band) is related to the defects and

disorders in structures in carbonaceous solid. A higher IG /ID value indicates a higher degree of graphitization [21]. For the carbon spheres prepared in the present study, the IG/ID value is about 1.24, which reveals the graphitization of our product is not high.

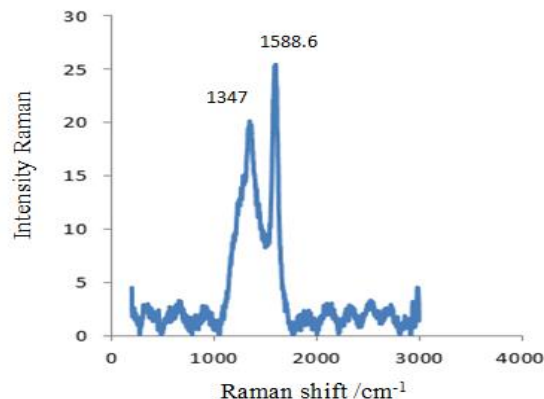


Fig 5. Raman spectrum of carbon nanospheres (CNS) produced by the pyrolysis of crude oil

X-ray Diffraction (XRD)

To confirm the degree of graphitization that has taken place in producing the CNS, an XRD study was undertaken. The results of the XRD study are presented in fig.5. Inspection of the XRD pattern reveals two dominant peaks, which are the characteristic peaks of amorphous carbon corresponding to (002) and (100) lines, respectively. The diffraction peak at about 24° corresponds to the structure factor peaks of graphite for the (002) plane reflections. The broadness of the peak is indicative of only a short-range structural order. An ill-defined peak at 43.57° can be assigned to the (100) graphite plane.

The peak at 2θ = 25.079° is used to calculate the mean crystallite size with Scherer's formula. The mean size of CNSs is approximately 311, 5 nm. These results are similar to those reported by Qian and Han, who produced CNS by pyrolysis of toluene [6].

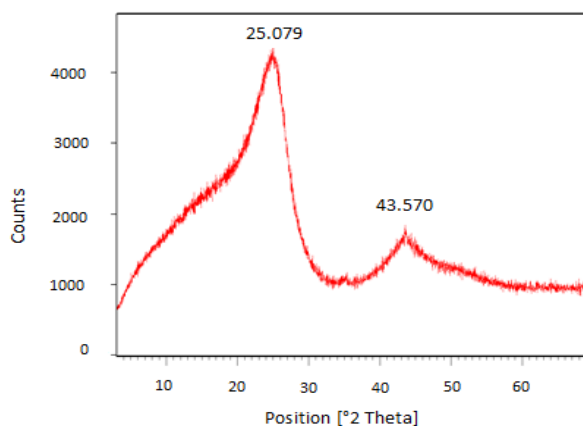


Fig 6. X-ray diffraction spectroscopy pattern of carbon nanospheres (CNS) produced by the pyrolysis of crude oil

Fourier transform infrared spectroscopy (FTIR)
The FTIR used to characterize these carbon structures using the vibrational frequencies. The FTIR spectrum in fig.7 a) showing the characteristic peaks of C=C of graphene materials at the peak 1629 cm⁻¹. The absorption peak at 749 cm⁻¹ corresponds to the C-H aromatic, and the peaks at 2923 and cm⁻¹ assigned as CH₂ asymmetric stretching vibration and CH₃ symmetric stretching vibration respectively. They play important roles in the formation process of spherical structures. The peaks 1716 due to the stretching vibration of carboxylic group. A broadened peak centered at 3432 cm⁻¹ is present in the samples, which is assigned to the (O-H) stretching vibration of

the carboxylic acid. These results indicate that there are a large number of residues including hydroxyl and carbonyl, carboxyl groups; they provide a potential avenue to load other molecules, functional groups after purification.

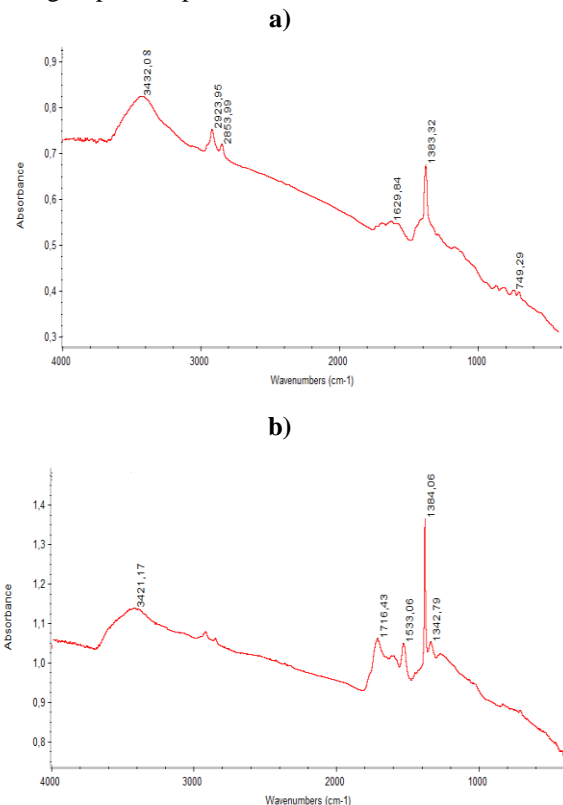


Fig 7. FTIR spectrum of carbon nanospheres (CNS) produced by the pyrolysis of crude oil, a) before purification of CNS, b) After purification

Model establishment and analysis

The response to each of the experimental conditions in terms of the yield CNSs reported in Table 2, MODDE 6.0 model used as experimental design and a statistically practicable second order polynomial equation was fitted to model the exhibited response-variable relationship.

Based on the experimental results listed in Table 2, an empirical expression (Eq.2) proposed by the software given as follow:

$$Y = 12.1955 + 0.367911 X_1 - 0.350085 X_2 - 0.726415 X_3 - 1.81205 X_1^2 - 0.745346 X_2^2$$

ANOVA analysis for response surface quadratic model of yield showed in Table 3. It is found that the model is considered to be statistically significant because the associated Prob.>F P value for the model is lower than 0.05 with a correlation coefficient of R^2 of 0.965 and the validity model of 0.35 is greater than the minimum required value of 0.25.

The significance of the process variables is based on the P value, with a value larger than 0.05 indicating the parameter to be insignificant, the significance test of regression Eq.2 shows that the influence of factors X_1 , X_2 and X_3 on yield CNSs synthesized are significant along with the interaction effects of X_1^2 and X_2^2 , while the effects of X_3^2 , X_1X_2 , X_2X_3 and X_1X_3 on yield are not significant.

Fig.8 shows the predicted vs Experimental CNS yield, which indicates the appropriateness of the model as the experimental data are in close agreement with the model equation.

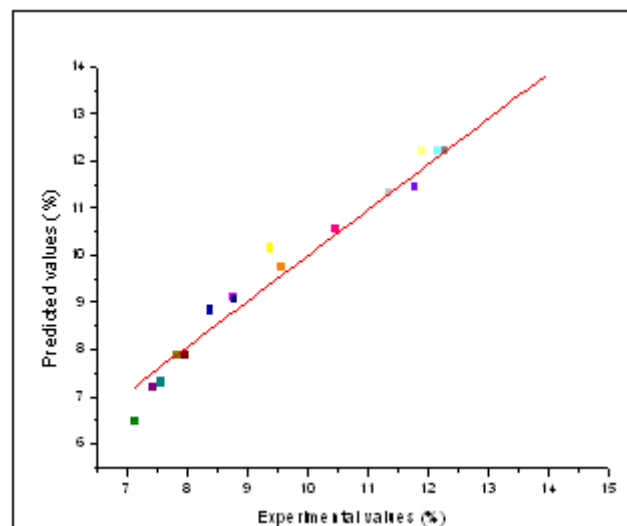


Fig 8. Predicted vs. experimental yield of CNSs synthesis Analysis of contour and response surface plots

The three-dimensional response surface plots constructed by using the statistical software to illustrate the interaction effects of selected factors on the percentage of CNSs and finally find out the optimal parameters for synthesis of carbon Nanospheres with a high quantity.

The influence of each variable on yield given below:

Effect of temperature and reaction time

RSM used and results are shown in the form of 3-D plots. Fig. 9 illustrates the effect of the temperature of reaction and process duration on the yield CNSs synthesized; the mass ratio (catalyst/crude oil) was kept constant. It can be seen that there is a linear trend between reaction time and reaction temperature from 860 °C, 90 min to 900°C, 120 min and the carbon yield increased with the increased of synthesis temperature and duration of synthesis. Beyond 900 °C, some parasitic phenomena occurs which are responsible for deactivation of the catalyst and the carbon yield decreased with the increase of synthesis temperature from 900°C to 940°C, at 900°C the carbon yield for 120 min deposition time is approximately 13%. When the reaction temperature is greater than 900°C, the deposit is included in encapsulated iron particles and catalyzed crude oil.

Also, same process occurred at 900°C by changing the time, the carbon yield reported at 900°C and for 120min, is 9,57%, for 150min, is 8,78%, the carbon yield decreased

With the increase of time from 120min to 150 min because of deactivated catalyst, it can be concluded that the interaction of reaction temperature and deposition time is insignificant.

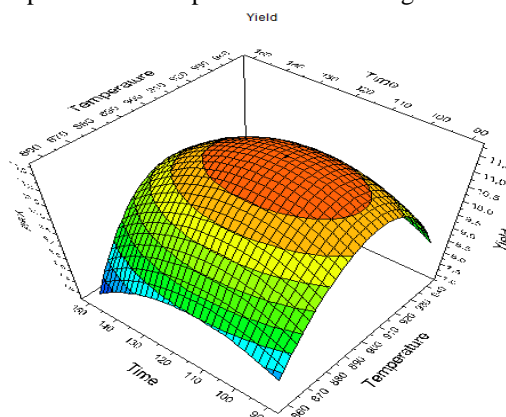


Fig 9. Three-dimensional response surface plot of CNS yield (effect of reaction temperature and process time, mass ratio (catalyst/crude oil 0.002 g/g)

Table 1 - Different variables and levels used in the experiment study

Factors	Code	Levels		
		-1	0	1
Temperature (°C)	X_1	860	900	940
Reaction time(min)	X_2	90	120	150
Mass ratio catalyst/crude oil(g/g)	X_3	0,00083	0,001655	0,00248

Table 2. MODDE 6.0 design matrix for the variables with the observed response for CNSs synthesized

Experimental run	Variables			Response Yield (%) of CNSs
	Temperature (°C), X_1	Reaction time (min), X_2	Mass ratio catalyst/crude oil (g/g), X_3	
1	860	90	0,00083	8,76
2	940	90	0,00083	9,38
3	860	150	0,00083	7,835
4	940	150	0,00083	8,78
5	860	90	0,00248	7,42
6	940	90	0,00248	7,95
7	860	150	0,00248	7,12
8	940	150	0,00248	7,55
9	860	120	0,001655	8,38
10	940	120	0,001655	9,57
11	900	90	0,001655	11,78
12	900	150	0,001655	10,47
13	900	120	0,00083	13,97
14	900	120	0,00248	11,35
15	900	120	0,001655	12,28
16	900	120	0,001655	11,9
17	900	120	0,001655	12,17

Table 3. Analysis variance for the significance parameters of quadratic model for Yield CNSs

Yield	Coef. SC	Std error	P
Constant	12.19550	0,253100	4,33858e-010
X_1	0,3679110,1478730,0417172		
X_2	-0,3500850,147873	0,049791	
X_3	-0,7264150,1478730,00172848		
X_1^2	-1,8120500,225851	8,94796e-005	
X_2^2	-0,7453460,225851	0,0131178	
X_3^2	0,01622980,2258510,944724		
X_1X_2	0,02202010,130703 0,870974		
X_1X_3	-0,05920930,1307030,664251		
X_2X_3	0,08073990,1307030,556303		
	N=17	DF = 7	$Q^2 = 0.857$ $R^2 = 0.965$ $R^2 \text{ adj} = 0.920$

Table 4. Optimal yield of CNSs synthesis conditions for the model

Temperature X_1 (°C)	Reaction time X_2 (min)	Mass ratio catalyst/crude oil X_3 (g/l)	Yield of CNSs synthesis	
			Predicted value	Experiment value
904	113	0.0008	13. 2354	13.05

Effect of temperature and mass ratio (Catalyst/crude oil)

Fig.10 represents the influence of temperature of reaction and amount of catalyst on the percentage of CNSs synthesized under reaction time constant(120 min). As can be seen that, when the reaction temperature increases from 860 to 900 °C and mass ratio (catalyst/crude oil) decreases, indeed the fusion of catalyst requires a high temperature (stage preliminary before the nucleation of the carbon nanospheres and their growth).The yield of CNSs increases, more than 900°C, and the carbon yield decreased;the deposit is included in encapsulated iron particles and deactivation of catalyst

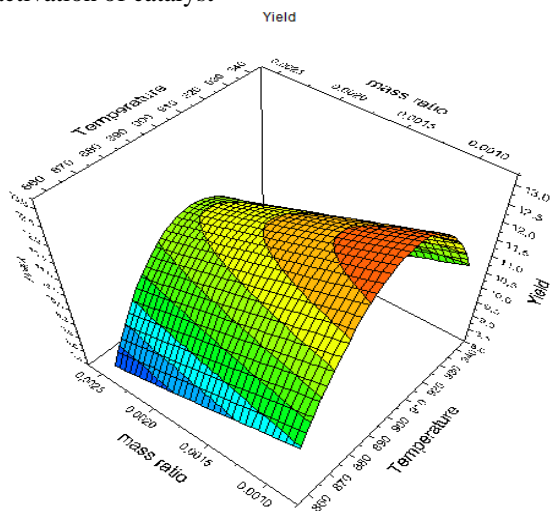


Fig.10:Three-dimensional response surface plot of CNS yield (effect of reaction temperature and mass ratio (catalyst/crude oil), process time(120 min)

Effect of reaction time and mass ratio (catalyst / crude oil)

The effect of reaction time and quantity of catalyst has been analyzed (Fig.11) , the carbon yield increased with the decreased of concentration of catalyst in crude oil and increased of duration of synthesis from 90 min to 120 min . More than 120 min in spite of a weak catalyst concentration, the carbon yield decreased; this is due to the formation of secondary products and deactivation of actives sites of catalyst.

Catalyst concentration is a key parameter, The concentration of catalyst particles in carrying gas must be weak in order to avoid their enlargement and their solidification.

Indeed, when the catalytic particle is solidified, additional carbon segregation led to a rapid encapsulation of the particle and its deactivation. This phenomenon is irreversible [22].

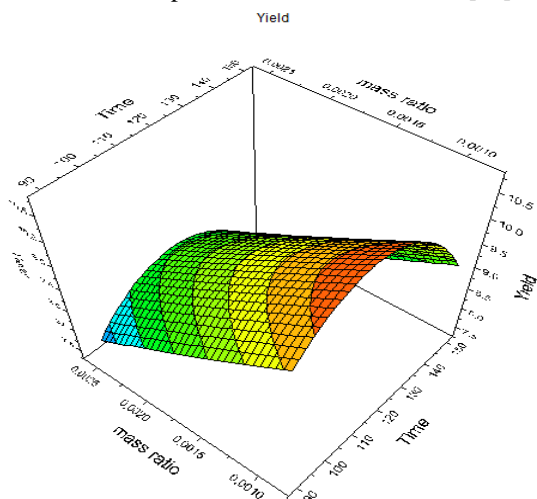


Fig 11. Three-dimensional response surface plot of CNS yield (effect of process time and mass ratio (catalyst/crude oil), reaction temperature (900°C).

Based on the experimental data above design is employed to optimize reaction temperature and process time, mass ratio (catalyst /crude oil) and the results shown in table 4.In order to validate the optimized process conditions, the experiments were repeated at the nearest possible experimental condition and the results were found to be in close agreement with the optimized values, vouching the validity of optimization under the optimized conditions, the CNS yield is 13.05 % for 113 min.

The CNS with high purity have been successfully obtained by CVD method using Algerian crude oil as a carbon source, the product is characterized by scanning electron microscopy (SEM) , XRD , Raman spectroscopy and FTIR spectrum .

Conclusion

The CNS are clearly observed by SEM, these CNSs have smooth surfaces and uniform particles with a diameter lower than 500 nm. Raman spectroscopy, XRD analysis indicated a degree of graphitization in the CNS is not high, FTIR proved the presence of new functions after samples treatment such as acid function.

Optimization of the process parameters of the CNSs synthesis was attempted using response surface methodology (RSM), the optimization was performed to optimize the response variable such as the yield of CNSs synthesized and we can concluded that :

Three factors interaction model and quadratic model were found to relate the process variables(reaction temperature , mass ratio(catalyst/crude oil) and process time) and the response variable(CNSs yield) effectively with the corresponding correlation coefficient of 0.96

The influences of factors X_1 (reaction temperature), X_2 (process time) , X_3 (mass ratio catalyst/crude oil) , X_1^2 and X_2^2 on the yield of CNSs were all found to be significant ,while the interaction effects of X_1X_2 , X_2X_3 , X_1X_3 and X_3^2 were found insignificant on yield.

Finally , the optimum values of synthesis parameters were obtained based on the experimental data which were 903°C , 113 min ,0.0008 g/g for the reaction temperature , the process time and mass ratio (catalyst/crude oil), respectively, for reach a yield of 13.05%.

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References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, Nature 318, 162, (1985).
- [2] A. K. Nebil, U. G. Esteban, A. B. David, G. H. Adrian, U. Sigita, C. Stefan, Chem. Mater. 19, 2304, (2007).
- [3] W. Qian, L. Z. Wei, F. Y. Cao, Q. W. Chen, Carbon 44, 1303, (2006).
- [4] S. Yang, X. Chen, S. Motojima, Diamond Relat. Mater. 13, 2152, (2004).
- [5] B. Basavalingu, K. Byrappa, M. Yoshimura, P. Madhusudan, A. S. Dayananda, J. Mater. Sci. 41, 1465, (2006).
- [6] Hai-sheng Qian , Feng-mei Han, Bing Zhang, Yan-chuan Guo, Jun Yue^a, Bi-xian Peng , carbon 42, 761-766 (2004).
- [7] Mitsue Fujita, Naoki Komatsu, Takahide Kimura, ultrasonics sonochemistry 21,943-5, 2014
- [8] Deshmukh AA, Mhlanga SD, Coville NJ. Mater Sci Eng R ,2010.
- [9] Sun X, Li Y. Angew Chem ,2004.
- [10] Pandurangappa M, Ramakrishnappa T. J Solid State Electrochem ,2010.

- [11] Yanyan Feng, Wen Yang, Ning Wang, Wei Chu, Daijun Liu, Analytical and applied pyrolysis, 2014
- [12] Hu Y, Liu Y, Qian H, Li Z, Chen J. 26 ,18570-18575, Langmuir 2010.
- [13] Z.H.Yi,Y.G.Liang,X.F.Le,C.W.Wang,J.T.Sun, Mater lett 61 ,2007
- [14]A.NietoMarquez, I.Espartera, J.C.Lazo, A.Romero, J.L.Valverde, chem Eng J 153, (2009).
- [15]P.Serp, R.Feurer, Y.Kihn, P.Kalck, J.L.Faria, J.L.Figueiredo, J.Mater Chem, 11, (2001).
- [16] Neil J. Colville, Sable D. Mhlanga, Edward N. Nxumalo, Ahmed Shaikjee, South African.sci 107.44, (2011).
- [17] X. Ma, F. Xu, L. Chen, Y. Zhang, Z. Zhang, J. Qian, Y. Qian, Carbon 44 (2006).
- [18] Ahmed Shaikjee, Neil J. Coville, carbon, Advanced Research, 195-223,(2012)
- [19]Azargohar, R., Dalai, A.K., Microporous Mesoporous Mater. 85, 219–225, (2005).
- [20] Arash Arami-Niyaa, Wan Mohd Ashri Wan Dauda, Farouq S. Mjalli, Faisal Abnisaa, Mohammad Saleh Shafeeyana, Chem Eng 90, 776-784, (2012).
- [21]. Yi Zheng Jin, Chao Gao, Wen Kuang Hsu, Yanqiu Zhu, Andrzej Huczko, Michal Bystrzejewski, Martin Roe, Chi Young Lee, Steve Acquah, Harold Kroto, David R.M. Walton, Carbon 43, (2005).
- [22] Jost O. , Gorbunov A. A. , Moller J. , Pompe W. , Graff A. ,Friedlein R., Liu X., Golden M. S., Fink J, Chem, Phys.lett. 339, 297-304, 2001.