Synthesis and Characterization of Tri-Composite Activated Carbon

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Abstract

Activated carbon loading with metals oxides is new adsorbents and catalyst, which seem very promising for desulfurization process. The present study deals with the preparation of three metals oxides loaded on activated carbon (AC). The tri composite of ZnO/NiO/CoO/AC was characterized by X-Ray Diffraction (XRD), X-Ray florescence (XRF), N_2 adsorption for BET surface area, pore volume and Atomic Force Microscopy (AFM). The effect of calcination temperature is investigated. The best calcination temperature is $250^{\circ}C$ based on the presence of phase, low weight loss and keep at high surface area. The surface area and pore volume of prepared tri composite are $932.97 m^2/g$ and $0.6031 cm^3/g$ respectively. The average particle size of tri-composite is 104.72 nm. Results confirmed a successful route for preparing the composite with promising characteristics.

Key words: Activated Carbon; Loading; Characterization, Calcination

Introduction

Activated carbon (AC) is one of the most known adsorbents due to its nature porous structure that have high surface area, large pore volume and its activity, due to this specific characteristics activated carbon can be used as adsorbent, catalyst and catalyst support for the removing different types of compounds [1] in addition activated can be regeneration for more than four times [2]. It was found that activated carbon was the best adsorbent between the activated alumina and nickel-silica alumina to remove model sulfur compounds.

Hydrothermal technique is one of the best methods to produce pure fine oxide powders.

Roy and Somya (2000) presented many methods like; hydrothermal decomposition, hydrothermal metal oxidation, hydrothermal reaction, hydrothermal precipitation and hydrothermal hydrolysis, hydrothermal electrochemical, reactive electrode submerged arc, hydrothermal microwave, and hydrothermal sonochemical.

The ideal powders could be defined as the powders having the ultimate pronounced properties. Some of these are, particle size of nano or micro size,

Soft or no agglomeration, narrow particle size distribution, spherical shape, having good morphology, controllable chemical composition,

uniform microstructure and good crystallinity [3].

The problem of use the activated carbon in desulfurization process is it selectivity, the nature of activated carbon surface is hydrophobic, and can be adsorbed aromatic hydrocarbons that have the same structure of cyclic sulfur compound, since has been suggested the oxidation process to convert sulfides (not polar compounds) to sulfones (more polarity compounds) with reactive adsorption to enhances selectivity of sulfur compounds rather than other aromatic compounds with further improvement to increase the selectivity of activated for adsorption of cyclic sulfur compound was incorporated with metal oxides.

There are more researches for improvement activated carbon such as loading with metal oxide where this can increase the sulfur removal, since reactive adsorption by use metal oxides on the support activated carbon, the π-electron interactions where cycle sulfur compound interact with metals oxide on the catalyst support activated carbon.

The improvement of selectivity of activated carbon surface to adsorbed cyclic sulfur compounds (DBT and 4,6-DMDBT) for model diesel fuel with sulfur content 20 ppm at ambient conditions studied in packed bed column by deposited metal species like silver, nickel and cobalt, finding the metal enhance the sulfur removal, and cobalt supported with activated carbon is more active than silver [4].

The activity of activated carbon loaded with copper oxide and nickel oxide examined, the conclusion that the copper or nickel made the specific site more active for adsorption of sulfur compounds and it is more efficient than activated carbon surface alone, this can be explained by π-interaction and acid-base interaction between metal species and sulfur

compounds, that convert at surface of active site then adsorbed on activated carbon surface [5].

The activated carbon and metals oxides composites prepared by thermal co-precipitation and examined its activity with sulfur compounds such as thiophene, benzothiophene and dibenzothiophene, and founded that metals oxides enhanced the interaction with sulfur compounds [6].

The employed of carbon nanotube, graphene oxide and activated carbon, investigated loaded with aluminum oxide at the loading ratio of 18.8% and 9% as adsorbents for DBT that dissolved in n-hexane as model diesel fuel with sulfur continent 250 ppm at 25°C, 200 rpm shaking speed with 2 h contact time in batch experiment, the highest removal of DBT near 98% for model fuels and 30% for real fuels at higher concentration was achieved using the activated carbon loaded the aluminum oxide with loading ratio of 9%, and BET surface area 825 m^2/g with pore volume 0.39 cm^3/g [2].

The adsorption of benzothiophene sulfone and dibenzothiophene sulfone dissolved in toluene with sulfur content 500 ppm for model diesel fuel studied by employing granular activated carbon supported with metal oxide (nickel oxide, iron oxide (III) and copper oxide) in batch process at room temperature and 120 rpm agitation speed, the highest activity of metal oxide to adsorbed benzothiophene sulfone founded for iron oxide 71.9% and the lowest for nickel oxide 65.4%, whereas for dibenzothiophene sulfone, highest removal for nickel oxide 99% and lowest for copper oxide 98.3%. [7].

It was found that activated carbon was the best adsorbent between the activated alumina and nickel-silica alumina to remove model sulfur compounds.

Hydrothermal technique is one of the best methods to produce pure fine oxide powders. Roy and Somya 2000 presented many methods like; hydrothermal decomposition, hydrothermal metal oxidation, hydrothermal reaction, hydrothermal precipitation and hydrothermal hydrolysis, hydrothermal electrochemical, reactive electrode submerged arc, hydrothermal microwave, and hydrothermal sonochemical. The ideal powders could be defined as the powders having the ultimate pronounced properties. Some of these are, particle size of nano or micro size, Soft or no agglomeration, narrow particle size distribution, spherical shape, having good morphology, controllable chemical composition, uniform microstructure and good crystallinity [3].

The aim of present work was prepared and characterized tri-metals oxides loaded on activated carbon surface and examined the best calcination temperature.

Experimental

Materials

The materials compounds which are used are activated carbon was supplied by Thomas Baker/India, Table 1 list the properties of activated carbon. Zinc nitrate hexahydrated $Zn(NO_3)_2.6H_2O$ with purity 98% was supplied by Thomas Baker, India and sodium hydroxide with purity 99% pellets was supplied by Hopkin and Williams, England nickel nitrate hexahydrated $Ni(NO_3)_2.6H_2O$ with purity 99.7% was supplied by Fisher Certified, cobalt nitrate $Co(NO_3)_2$ was supplied by Panreac, Espana and Kerosene with sulfur content 2850 ppm was supplied by the Midland Refineries Company/Al-Dura Refinery.

Table 1, Properties of AC

Property	Value
PH for AC dispersed in deionization water	5-7
Real density, g/cm3	2.5841
Bulk Density, g/cm3	0.2662
porosity εp	0.89

Procedure of Preparation

Zinc oxide, nickel oxide and cobalt oxide loaded on Activated carbon was prepared by co-precipitation method. 10g of activated carbon we added 0.4917 g, 0.4917 g and 0.5382 g of zinc nitrate hexahydrated, nickel nitrate hexahydrate and cobalt nitrate respectively to obtain ≈ 3 wt.% loading for each oxide. First activated carbon is dried in furnace for 1 h at 200°C, and then 10 g of activated carbon powder was dispersed in 250 ml deionized water for best dispersion.

The solution of activated carbon and deionized water was mixed by putting a magnetic stir bar with magnetic stir plate for 12 h. weighted a 0.4917 g of zinc nitrate hexahydrate and dissolved in 20 ml water, weighted 0.4917 g of nickel nitrate hexahydrate and dissolved in 20 ml water and also weighted 0.5382 g of cobalt nitrate and dissolved in 20 ml water.

Then addition zinc nitrate solution by drop wise in dispersed activated carbon and water followed by adding nickel nitrate solution and cobalt nitrate solution while stirring the mixture, the ph of mixture is ≈ 5.7.

The pH of the mixture adjustment by adding 1M of NaOH solution until the PH reaches to 8. Heating the mixture for 6 h at 90°C with reflux and under mixing, followed by filtration, washing, drying overnight at 110°C and calcination the product for 3h at different calcination temperatures (150-350°C).

Results and Discussion
Characterization of Tri-Composite
The XRD patterns of the activated carbon, showed the peaks between 2θ= 20-30 and 40-50, which are noisy and disordered indicating the amorphous carbon as shown in Figure 1. For AC/ZnO/NiO/CoO, the clear peaks at 2θ =31.748°, 34.438°, 36.249°, 47.539°, 56.551°, 62.856°, 67.912°, 69.052°, 72.604° and 76.950° indicates to crystalline ZnO, and at 2θ = 37.278, 43.295, 62.913, 75,439, and 79.387 indicate to crystalline NiO, and at 2θ = 42.644°, 49.662°, 72.864° indicate to crystalline CoO as shown in Figure 2 and noisy background patterns refer to amorphous carbon.
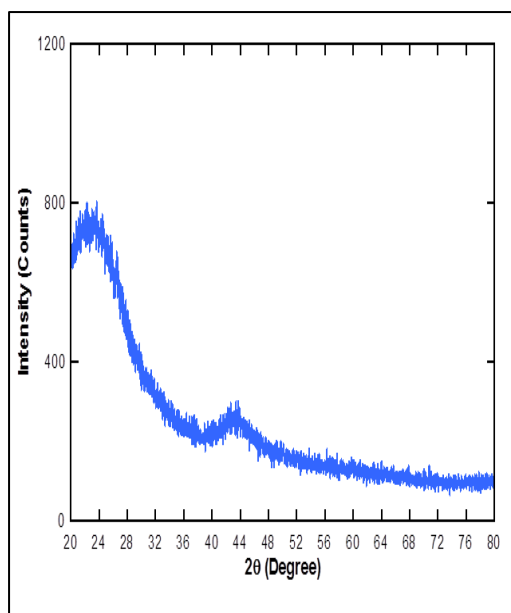

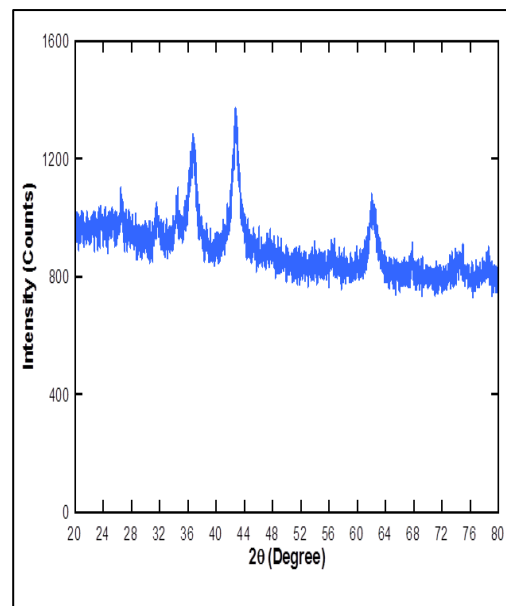Fig. 1, XRD Pattern of activated carbon

Fig. 2, XRD Pattern of Tri-Composite

The XRF analysis shows the metal oxide composition for metals oxides loading on the surface of the activated carbon. A total measured metals oxides for each composite was ≈ 10 wt. %. The loading ratio was chosen 10wt % because the increasing in loading ratio causes the block of pore, and leads to decrease of surface area [8].

The average particles diameter was determined by AFM. Table 2 list the particles size distribution of activated carbon and prepared composites. The increasing in particle size causes the decrease in the surface area.

Figure 3 was showed topographical surface images of activated carbon and its composites in two dimensional (2D) and three dimensional (3D) were obtained from AFM analysis. Table 3 shows the results of AFM measurements.

The most important parameters in AFM are the average roughness, root mean square roughness, surface skewness and surface kurtosis. The results indicated that the tri-composite is roughness than activated carbon because of the mechanism of nucleation.

The results show that both activated carbon and tri-composite have negative surface skewness (Rsk<0 : Skewed upward relative to the average line) which means that surface has more valleys than peaks. The results show also that both activated carbon and tri-composite have surface kurtosis are lower than 3 (Rku<3 : The height distribution is not sharp) indicating a flat surface (platykurtic) [9, 10].
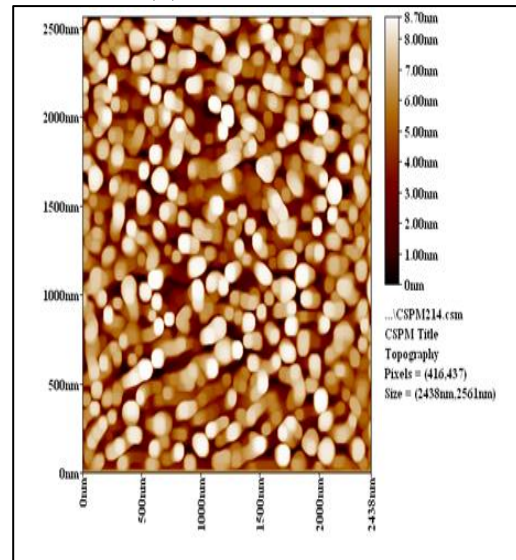
Table 2, particle size distribution

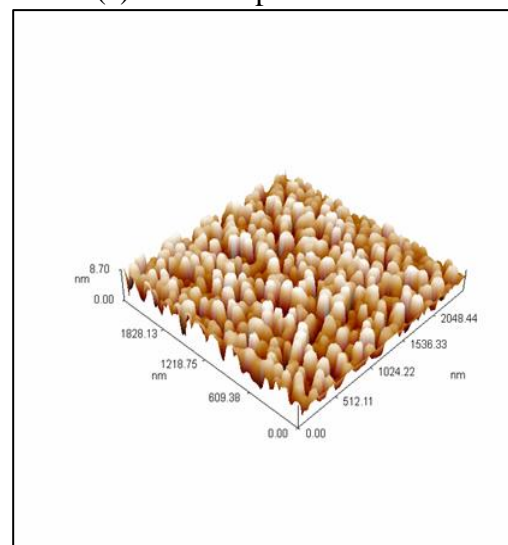| Composite Type	Avg. Diameter [nm]	≤ 10vol % [nm]	≤ 50vol % [nm]	≤ 90vol % [nm]
AC	93.84	50	90	140
Tri-Composite	104.72	70	100	130
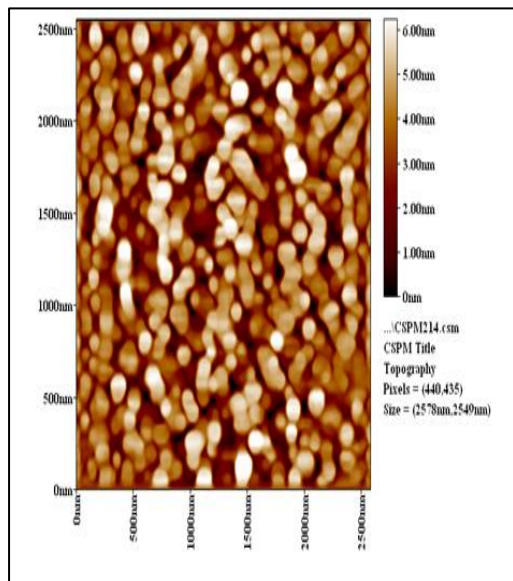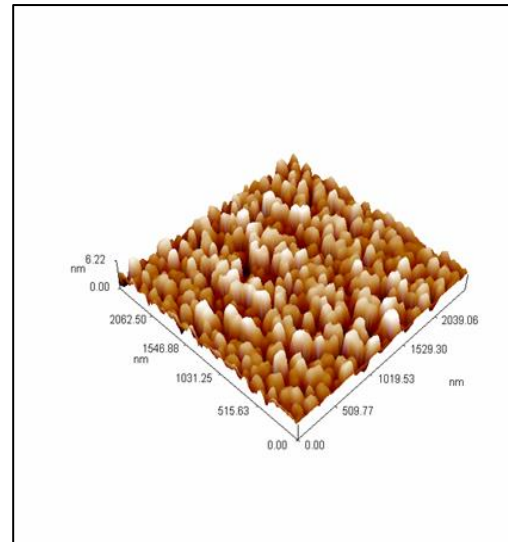
(b) AC surface 3D

(c) Tri-Composite surface 2D

(a) AC surface 2D

(d) Tri-Composite surface 3D
Fig. 3, AFM of AC and Tri-Composite surfaces 2D and 3D

Table 3 AFM Roughness Analysis Measurements

| Roughness (2D) Parameter		Activated Carbon	Tri-Composite
Amplitude Parameter			
Maximum height of the roughness profile (R_z)		6.21 nm	5.59 nm
Average roughness (R_a)		1.17 nm	1.79 nm
Root mean square deviation of the roughness profile (R_q)		1.42 nm	2.14 nm
Skewness of the roughness profile (R_{sk})		-0.315	-0.552
Kurtosis of the roughness profile (R_{ku})		2.43	2.37
Hybrid Parameters			
Root mean square slope of the roughness profile ($R\Delta q$)		0.0711 nm^{-1}	0.138 nm^{-1}
Surface Area Ratio (R_{dr})		0.248	0.918
Functional Parameter			
Surface Bearing Index (S_{bi})		2.38	8.17
Core fluid Retention Index (S_{ci})		1.38	1.2
Reduced summit Height (S_{pk})		0.545	0
Core roughness depth (S_k)		3.8 nm	5.32 nm
Reduced valley depth(S_{vk})		1.54 nm	2.65 nm
Height interval of bearing curve (S_{dc})	(0-5)%	0.607nm	0.263nm
	(5-10)%	0.328nm	0.246nm
	(10-50)%	1.64nm	2.22nm
	(50-95)%	2.79nm	4.45nm
Spatial Parameter			
Fractal dimension		2.55	2.48

Calcination Temperature Study

The influence of calcination temperature on the weight of activated carbon loss as well as the existence of phases has been studied. The vacuum condition or N_2 space is perfect to flash out air, since they prevent carbon from weight loss in the combustion as seen in Equation (1).

$$AC + O_2 \rightarrow CO_2 + CO \qquad \dots (1)$$
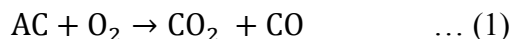
The selection of the calcination temperature ranges between 150-350°C according to the previous studies. Figure 3 shows TGA curves of AC and Fe_2O_3/ AC [11].
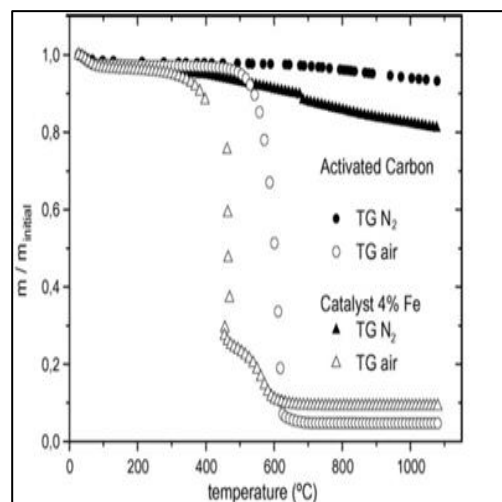
Figure 4 TGA Curves of AC and AC/Fe2O3[11]

As shown in Figure 4 the activated carbon is thermally stable up to 550°C, while the Fe$_2$O$_3$/AC began to burn approximately at 350°C. Also, the presence of nitrogen was beneficial for both materials because they were more stable reaching temperatures higher than 600°C.

By considering these findings, the effect of calcination temperature on ZnO/NiO/CoO/AC was studied.

5 g of AC/ZnO/NiO/CoO was taken and calcinated at different temperatures ranged between 150-350°C, and weighted after calcination as listed in Table 4.

Table 4, Weight loss and Surface Area at Different Calcination Temperature

Temperature ^{o}C	Wt%	Surface area m^2/g 3h calcination
150	98.35	839.709
200	36.73	881.116
250	29.88	604.6587
300	21.61	345.0581
350	18.92	299.218

The surface area decreases as a result of the loss of activated carbon and the increase of loading metals oxides. To select the best calcination temperature, the phases must be checked in addition to the decrease in surface area.

Therefore, by examining Figures 5 to 7 for the XRD pattern at different calcination temperature it was concluded that the best calcination temperature is 250°C.

The surface area and pore volume of prepared tri composite at best calcination temperature for 10g sample were measured by BET method, the resulted values of surfaces area and pore volume listed in Table 5.

Table 5, surface area and pore volume

	AC	Tri-Composite
Surface Area m^2/g	1005.5	932.98
Pore Volume cm^3/g	0.6203	0.6031

The surface area of activated carbon after loading of ≈10wt % metals oxides still high and near from the values of original source, and sometimes the surface area and pore volume increase or still the same or near from original source in case loading ratio less or equal 10 wt. % , this due to good dispersion of the metals oxides [12].
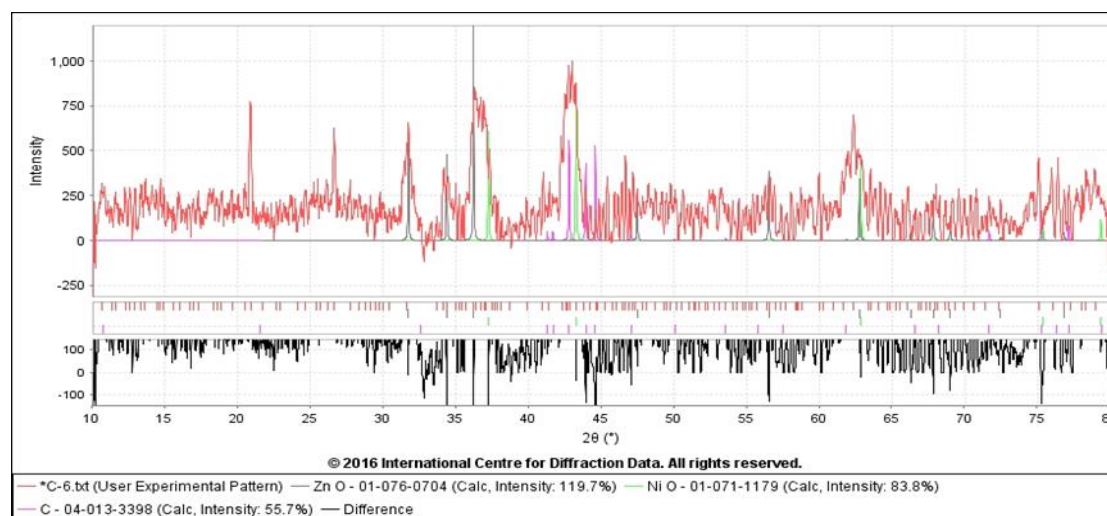
— *C-6.txt (User Experimental Pattern) — Zn O - 01-076-0704 (Calc, Intensity: 119.7%) — Ni O - 01-071-1179 (Calc, Intensity: 83.8%)
— C - 04-013-3398 (Calc, Intensity: 55.7%) — Difference

Fig. 5, XRD Test of at Calcination Temperature 350°C

— *C-8.txt (User Experimental Pattern) — Zn O - 04-006-7189 (Calc, Intensity: 56.39999999999999%) — Ni O - 01-071-4750 (Calc, Intensity: 76.5%)
— C - 04-006-5764 (Calc, Intensity: 34.2%) — Co O - 04-008-2749 (Calc, Intensity: 95.6%) — Difference
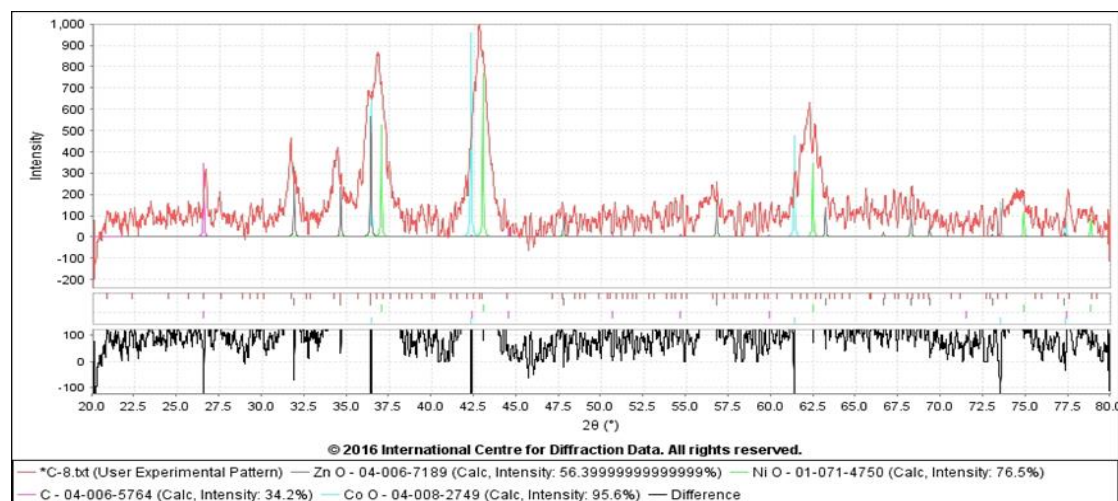
Fig. 6, XRD Test of at Calcination Temperature 300°C

— *C-7.txt (User Experimental Pattern) — Zn O - 04-005-5076 (Calc, Intensity: 80.10000000000001%) — C - 04-016-6288 (Calc, Intensity: 45.6%)
— Ni O0.96 - 01-078-4380 (Calc, Intensity: 62.3%) — Co O - 04-008-2749 (Calc, Intensity: 65.60000000000001%) — Difference
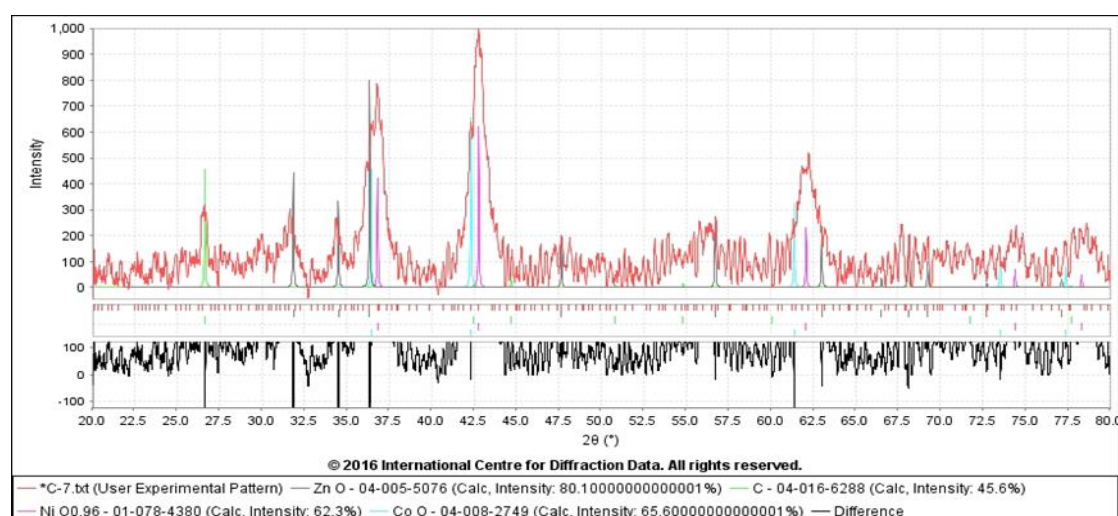
Fig. 7 XRD Test of at Calcination Temperature 250°C

Activity of Tri-Composite

The activity of tri-composite is examined for oxidation desulfurization of Iraqi kerosene fuel with sulfur content 2850 in bench scale at ambient conditions (6.25g ZnO/NiO/CoO/AC, 25°C and 40 min) using oxygen gas, the samples was test after filtered from composite. The oxidation desulfurization experiments were carried out in 500 ml flask; oxygen gas was bubbled at constant flow rate. The sulfur content of kerosene filtered was determined according to ASTM D-7039 in the Petroleum Research and Development Center / Ministry of oil by using the testing device (Sulfur analyzer, Sindie OTG, USA). The total sulfur content determined is 2008 ppm,

the sulfur removal percent 29.54%, the percent removal of sulfur compounds was calculated using equation (2).

$$\% \text{ Sulfur Compounds Removal} = \frac{C_0 - C_t}{C_0} * 100 \quad \dots (2)$$

Conclusions

The best calcination temperature is 250°C; it was checked with crystal phase, weight loss and surface area.

The observation by atomic force microscopy in both surface morphology and surface growth characterization shows the tri-composite is roughness than activated carbon because of the mechanism of nucleation; both activated carbon and tri-composite have more valleys than peaks in their surfaces and both activated carbon and tri-composite

have a flat surface. The particle size distribution for tri-composite: ≤ 10 vol. % 70 nm; ≤ 50 vol. % 100 nm and ≤ 90 vol. % 130 nm.

The surface area and pore volume of prepared tri composite are 932.97m^2/g and 0.6031cm^3/g respectively. The oxidation desulfurization of Iraqi kerosene fuel using oxygen gas and tri-composite gives 29.54% sulfur removal.

Nomenclature

Greek Letters		
θ	Scattering or Bragg angle	
ε_p	Porosity of the composite particles	
Notations		
Symbol	Definition	Units
C_0	Initial Sulfur compounds Concentration	ppm
C_t	Sulfur compounds Concentration at any time	ppm
Abbreviations		
AC	Activated Carbon	
ZnO/NiO/CoO/AC	Zinc Oxide /Nickel Oxide/Cobalt Oxide/Activated Carbon	
AFM	Atomic Force Microscope	
ASTM	American Standard Test Method	
BET	Beunauer, Emmett and Teller	
DBT	Dibenzothiophene	
4,6-DMDBT	4,6-Dimethyldibenzothiophene	
ODS	Oxidation Desulfurization	
ICDD	International Center for Diffraction Data	
TGA	Thermal Gravimetric Analysis	
XRF	X- ray Florescence	
XRD	X-Ray Diffraction	

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