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## Adsorptive Desulfurization of Gas Oil Over $\text{Cu}_2\text{O}/\text{AC}$ , $\text{ZnO}/\text{AC}$ and $\text{NiO}/\text{AC}$ Adsorbents

**Abstract-** In the present work, Iraqi gasoil fraction was treated by using three prepared metal-impregnated activated carbon adsorbents for sulfur removal using adsorptive desulfurization method. In the first experimental section, commercial activated carbon was loaded individually with copper, zinc and nickel oxides and reaches the form of  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$  and  $\text{NiO}$  respectively. XRD, BET, surface area and metal content were determined for the three prepared adsorbents. The three prepared metal loaded adsorbents were tested for sulfur removal from Iraqi gasoil fuel via batch mode and continuous mode. In continuous operation, fixed bed adsorber packed individually with the three prepared adsorbents was used and breakthrough curves were generated. The results of the present study indicate that the desulfurization enhanced when metals zinc, copper and nickel were loaded onto activated carbon surface. Sulfur adsorption uptake by the three adsorbents followed the order  $\text{Cu}_2\text{O} > \text{ZnO} > \text{NiO}$  (the highest desulfurization percent obtained via continuous mode for  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$  and  $\text{NiO}$  were 69.7%, 67.47% and 60.7% respectively). Moreover, it was exhibited that for batch mode experiments by increasing the adsorbent's concentration enhanced the sulfur removal by a noticeable amount. Whilst for the continuous mode experiments, it dealt mainly with contact time; thereby the maximum desulfurization percentage was obtained at the first 15 minutes.

**Keywords-** adsorptive desulfurization, activated carbon, gasoil, metal oxides, sulfur.

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### 1. Introduction

Since crude oil becomes the most important source of energy nowadays, it's essential to emphasize the necessity of treating it from its issues; such issues are illustrated by the impurities content in major products of petroleum. It became a priority to produce ultraclean transportation fuel, particularly, gasoline, diesel and jet fuels. The sulfur and Nitrogen content of these fuels may be serious environmental concerns, for the conversion of sulfur into toxic  $\text{SO}_x$  as well as  $\text{NO}_x$  emissions that occurred upon combustion in internal combustion engines [1].  $\text{SO}_x$  and other emissions resulted from combustion of sulfur-containing fuels leads to several hazards such as air pollution, acid rains formation, dry deposition, and smog, which considered being a primary human health and environment worries [1, 2].

Sulfur compound could cause a catalyst deactivation while using in crude oil processing. Also, it's a major cause of several corrosion problems in pumping, pipeline, parameter failure of combustion engines and causes poisoning of the catalytic converters that are used in automotive engines [2].

Currently, the main focus is on sulfur reduction in transportation fuels. The favorable sulfur content that must be reached is 15 ppmw for diesel oil, 30 ppmw for gasoline in USA and 10 ppmw for diesel

and gasoline in EU. For that, deep desulfurization is necessary to reach this amount of sulfur content [3].

Several methods have been applied for such aspect, including conventional catalytic hydrodesulfurization (HDS), adsorptive desulfurization, chemical oxidation, extractive desulfurization and photochemical desulfurization and biodesulfurization by using special bacteria. Traditional hydrodesulfurization process (HDS) has been worldwide available, it's carried out using catalysts at high temperature and pressure conditions. However, this process doesn't work efficiently in the ultra-deep desulfurization range to reach sulfur content 100 ppmw or less. Moreover, it considered an expensive process for the high cost of operation conditions in which illustrated by the high pressure of hydrogen gas and high temperature and expensive catalyst [4, 5]. Adsorptive desulfurization considered being an efficient and economical process for sulfur removal due to the availability of the required materials with no expensive conditions as in HDS. Moreover, it's more applicable for reaching the ultra-clean fuel by deep desulfurization [5-7]. Many kinds of porous solid materials such as wide types of zeolite, alumina, silica and different metal-based adsorbents could be used as adsorbents for desulfurization process. Activated carbon considered being more effective than other

adsorbents including bentonite [6], metal oxides [2], montmorillonite-clay [5], and more, for the high surface area that activated carbon has, low cost, chemical, thermal and mechanical stability and its surface morphology which makes its adsorption capacity more efficient for obstinate organosulfur compounds. Several studies in previous works investigated the enhancement of activated carbon's capability of sulfur removal from liquid fuels.

Reference [8] prepared and tested the desulfurization capability of four metal-loaded polystyrene-based activated carbons as adsorbents including Na, Co, Cu, and Ag efficiently dispersed onto the carbon matrix to improve activated carbons for Dibenzothiophene (DBT) removal. The prepared adsorbents showed high adsorption DBT removal efficiencies. The metals loaded onto the activated carbons surface act as structural stabilizers of the AC materials and as catalytic initiation for reactive-adsorption in addition to provide active sites for selective adsorption of aromatic sulfur compounds. They stated that Co and Cu impregnated ACs showed the highest DBT uptakes compared with Na and Ag. The investigators proved that the presence of sulfur compound molecules in the acid groups in the AC surface which deposited from the sulfonic excess of the precursor solutions leads to specific sulfur-sulfur interactions leading to an improvement in the DBT adsorption capacity. Actually, they did not provide an explanation for the enhancement mechanism, instead of that they suggested that Cu acts as an activator for oxygen, and therefore enabling split the bonds of sulfur-carbon in the DBT molecules.

Reference [9] investigate the effects of several metals loaded onto activated carbons (ACs) on the activation-energy of dibenzothiophene desorption. Five metal ions were individually loaded on the ACs by impregnation technique including Ag, Zn, Ni, Cu, AC and Fe. They used Temperature programmed desorption, TPD tests to measure the TPD curves of dibenzothiophene (DBT) on these prepared adsorbents, and estimated the desorption activation-energy of (DBT) on the AC surfaces. The investigators discussed the variation of activation-energy of (DBT) on the ACs by using the principle of hard and soft acid and base, HSAB. Their results showed that new adsorption sites for (DBT) adsorption were generated when loading ACs loaded individually with Ag, Ni, Cu and Zn. The activation-energy of (DBT) desorption on the ACs, Ag/AC, Zn/AC, Ni/AC, Cu/AC, AC and Fe/AC were 93, 88, 75, 69, 54 and 47 kJ/mol respectively. In comparison with the original AC, the loading of Ag enhanced the

dibenzothiophene interaction with Ag/AC surfaces because Ag is soft-acid and dibenzothiophene is soft-base, also the dibenzothiophene interaction with Fe/AC surfaces was weak due to hard-acid Fe compared with soft-based dibenzothiophene. They stated that the loading of the acid-ion such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Ni}^{2+}$  on the AC surfaces could weaken the hard-acids locally in the adsorbents surfaces so that dibenzothiophene adsorption was improved to some extent.

Reference [10] evaluated the performance of several activated carbons on adsorptive desulfurization of model fuel and the real gasoil. The adsorption experiments have been carried out in a batch scale at ambient temperature and under the atmospheric pressure. They indicated that the most refractory organosulfur compounds, which cannot removed in the hydrodesulfurization process were selectively adsorbed and removed. They also found that the adsorbents affinities to DBT and 4,6-DMDBT were preferable and declared than the other aromatic compounds and 4,6-DMDBT has the highest selectivity over all the used adsorbents between the sulfur compounds. Regeneration of the used adsorbent was studied by washing the spent adsorbents with toluene and by heat treatment through heat treatment. A suggested adsorptive desulfurization process of sulfur compounds from petroleum fractions over CoMo/AC supported catalyst was also studied and discussed.

Reference [11] also investigated the adsorption of dibenzothiophene by metal based-activated carbons (ACs). Three types of adsorbents, Cu/AC, Ag/AC and Fe/AC were separately prepared by impregnation method with assisted of ultrasound irradiation technique using vinous metal salt. They measured individually the adsorption isotherms of dibenzothiophene on the metal based-ACs at different metal ions loaded on the ACs and the dibenzothiophene uptake was studied. Their results showed that the dibenzothiophene adsorption efficiency of the metal based-ACs by using impregnation without ultrasound irradiation technique followed the order: Ag/AC > Cu/AC > AC > Fe/AC and the metal impregnation was significantly enhanced the adsorption efficiencies of the of dibenzothiophene. They also indicated that using of ultrasound irradiation technique to prepare metal based-ACs improved the dispersion of metals particles onto ACs surface, make it finer, and therefore better results. As a result, the Ag/AC and Cu/AC prepared by using ultrasound irradiation method have higher adsorption efficiencies of dibenzothiophene than those prepared using impregnation only.

Reference [12] prepared and characterized three polymer-based activated carbons (ACs) loaded with Fe and different quantities of Cu on the ACs surface as adsorbents materials for removal of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from model diesel oil. They applied X-ray diffraction, XRD, scanning electron microscopy, SEM and thermal analysis, TA tests to characterize the original and supported ACs. The investigators indicated an enhancement in selectivity for DBT and 4,6-DMDBT adsorption due to loading of Fe and Cu species and the micropores volume is significant factor governing the amount of sulfur adsorbed.

Reference [13] prepared and used PdCl<sub>2</sub> supported on commercial microporous activated carbons (ACs) for adsorption and removal of benzothiophene (BT) and dibenzothiophene (DBT) from model fuel consisted of 500 ppm of BT and DBT solutions in n-hexane. They used the wet impregnation method to impregnate PdCl<sub>2</sub> in acidic media, and then dried the samples at 130 °C under Helium flow. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photo-electronic spectroscopy (XPS) and N<sub>2</sub>-adsorption isotherms. The results indicated that PdCl<sub>2</sub> was effectively supported on the AC as the chloride itself and as metallic phase and the adsorbed uptakes were measured by the concentration differences. In addition, the Fourier transform infrared spectra (FTIR) were measured upon benzothiophene vapors adsorption. They showed that PdCl<sub>2</sub> impregnated ACs improved sulfur adsorption capacities, and sulfur compounds with an increasing number of aromatic-rings were discriminatory adsorbed.

Reference [14] investigated the adsorption of sulfur compounds from model diesel fuel which consisted of various thiophenic compounds benzothiophene (BT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and dimethyldibentiophene (DMDBT) dissolved in n-hexane in single solute method by using impregnated activated carbons. Two types of activated carbon (prepared AC from palm seeds and commercial polyacrylonitril based activated carbon fiber (ACF)) were used and loaded with different copper and nickel species for that purpose. Laboratory prepared activated carbon, treated with hydrogen was loaded with Cu, Cu<sub>2</sub>O, CuO, Ni, NiO species to improve the morphology of the activated carbon and thereby the interaction between each species and thiophenic compounds. Results showed that the highest uptake of thiophenic compound was by the adsorbents

loaded with Cu<sub>2</sub>O and NiO. Adsorption uptake of thiophenic sulfur compounds showed a majority of adsorbents which followed the order of: 4,6-DMDBT > DBT > BT for the higher intensity of specific and non-specific interactions of larger thiophenic compounds molecules with metal loaded adsorbent. The present work deals with preparation of different metal-based activated carbons which including impregnated of copper, zinc and nickel metals onto commercial activated carbon to treat Iraqi gasoil fraction for sulfur removal by adsorptive desulfurization method.

## 2. Experimental

### I. Materials

Iraqi hydrodesulfurized atmospheric gasoil supplied by Al-Dura Refinery-Baghdad as a real fuel. The main physical properties of the gasoil fraction are listed in Table 1. Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99% purity), Zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99% purity) and Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 97% purity) supplied by Fluka Chemie AG company were used as copper, zinc, and nickel precursor respectively. Activated carbon pellets (AC) (supplied from Research Products International Corp. USA) of purity 99.9% was used as support material without any heat or chemical pretreatment. The surface area (BET) and pore volume were tested using sorption of N<sub>2</sub> and was found to be 1066 (m<sup>2</sup>/g) and 0.65 cm<sup>3</sup>/g respectively. The AC pellets was milled and sieved to size range of (0.3-0.6) mm before be impregnated.

### II. Methods of adsorbents preparation

Incipient wetness impregnation method (capillary impregnation) was used for adsorbent preparation. Activated carbon without any pretreatment was loaded with about 10 wt% metal individually using Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solutions as copper, zinc, and nickel precursor respectively. The experimental apparatus consists of a conical flask connected with a separating funnel, vacuum pump, magnetic stirrer and trap to absorb the moisture and gases. An impregnation aqueous solution was prepared by dissolving 15.7 g nickel nitrate, 12.3 g copper nitrate and 18.4 g zinc nitrate individually in 26 ml of distilled water with mixing at room temperature, and then this solution was transferred in the conical flask of the impregnation apparatus containing 40 g of dried activated carbon. The impregnation took place drop by drop for about 0.5 hour and then the samples were left over 24 hr at the ambient conditions to load the largest amount of metals precursor. The incipient wetness

impregnation procedure was illustrated in Figure 1. After impregnation, the three impregnated activated carbon samples were dried and calcined as shown in Table 2.

**Table 1: The properties of the Iraqi gasoil.**

Specification	Iraqi gasoil
Sulfur content , mg/l	990
Density at 15.6 °C	0.82
Flash point, °C	67
Pour point, °C	-20
Cetane No.	54
Viscosity at 40 °C , cst	2.3
Diesel index	60

**Table 2: Heat treatment conditions for activated carbon samples impregnated with nickel, zinc and copper species**

Adsorbent	Drying conditions	Calcination conditions
Cu <sub>2</sub> O/AC	90 °C, 6 hr	500 °C/vacuum for 3 hr
ZnO/AC	90 °C/vacuum, 6 hr	250 °C/vacuum for 3 hr
NiO/AC	90 °C/vacuum, 6 hr	500 °C/vacuum for 2 hr

### III. Absorbents characterization

X-ray powder diffraction (XRD) analysis was used to characterize the crystallinity of zinc, copper and nickel loaded onto activated carbon, using an XRD-6000 by changing the angle ( $2\theta$ ) within the range of  $20^\circ$  to  $80^\circ$ . X-ray diffraction analysis was achieved in department of earth Science/Baghdad University. The device used for analysis the X-ray is diffractometer type (Bruker D2 PHASER). The results of crystalline phases of each metal loaded onto activated carbon were characterized and compared with the standards of International Center for Diffraction Data, ICDD. Atomic absorption spectroscopy model (Varian AA240 FS) was used for determination the total content of metal species loaded onto activated carbon. The BET surface area and the pore volume of the original activated carbon and impregnated activated carbon was determined using Quanta chrome Autosorb gas sorption system estimated from nitrogen adsorption and desorption. The BET device was located in the Petroleum Research and Development Center/Ministry of Oil/Baghdad-Iraq. The sulfur content in model fuel and real gasoil was determined by X-ray fluorescence in the Petroleum Research and Development Center/Ministry of Oil/Baghdad by using Horiba sulfur-in-oil analyzer type (SLFA-2100).

### IV. Desulfurization procedure

The desulfurization experiments for gasoil were conducted to study the effect of adsorbent concentration in batch mode and also under fixed bed operation using adsorber column. In batch experiments 10 ml of gasoil was mixed with each adsorbent with different adsorbent concentration of 0.01- 0.08 g adsorbent/ml gasoil in twelve 100-ml flasks (four concentrations for each adsorbent's type). The flasks were then shaken for 5 hr at room temperature and constant shaking speed of 250 rpm.

The desulfurization experiments were also carried out in continuous process, in which a fixed bed of each adsorbent was filled in an adsorber column. Pyrex glass column of 15 mm (I.D.) and 25 cm in height was used as adsorber. The column was stuffed with about 1 cm height fiberglass at the bottom to support the adsorbent's bed. The adsorber column was filled with 6 g of each adsorbent individually giving a bed height of 5 cm and volume of about 9 ml. All fixed bed runs were carried out at room temperature and constant liquid hourly space velocity (LHSV) of  $3.5 \text{ hr}^{-1}$ . 1 L separatory funnel was used as gasoil feed tank also 50 ml burette was used as calibration tube to check the inlet flowrate. Both funnel and calibration burette was placed at the top of the adsorber column.

The gasoil feed was introduced to the adsorber column at constant flowrate and was allowed to pass through the bed of adsorbents in a down flow direction. The samples were collected at different time intervals for sulfur analysis until saturation of adsorbent's bed was achieved, which was noted by the stability of sulfur concentration with time and the adsorption dynamics. Therefore, breakthrough curves were generated by plotting the sulfur concentration vs. time.

The desulfurization percentages were calculated as the ratio of the sulfur concentration that was adsorbed by the adsorbent to the sulfur concentration present initially in the fuel according to equation bellow [13, 14]:

$$\text{Desulfurization}\% = \frac{C_{in} - C_{out}}{C_{in}} * 100 \quad (1)$$

The sulfur adsorption capacity (q) was calculated by using the following equation [14].

$$q = \frac{V_{sol}(C_{in} - C_e)}{m_{cat}} \quad (2)$$

Where q is the amount of sulfur adsorbed (mg /g cat.),  $V_{sol}$  is the volume of solution (L),  $C_{in}$  and  $C_e$  are initial and equilibrium concentrations (mg /l), and  $m_{cat}$  is the mass of adsorbent (g).

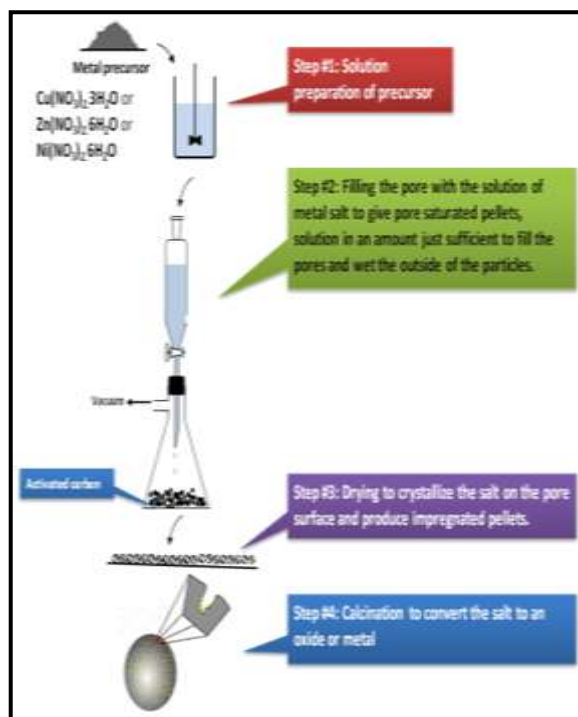


Figure 1: The incipient wetness impregnation procedure.

### 3. Results and Discussion

#### 1. Adsorbent characterization

Metal-based activated carbon samples were prepared by impregnation of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O onto AC in parallel and individually. For copper, AC was loaded firstly with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O then dried and calcined at 500 °C under vacuum. According to

thermal decomposition data of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O under vacuum [14, 15], it melts at 115-155 °C, then converted to β-Cu<sub>2</sub>(OH)NO<sub>3</sub> at 200-217 °C, by increasing the temperature it converted to CuO at 260–310 °C, finally CuO decomposes to Cu<sub>2</sub>O at > 450 °C as has happened in this research when using calcination temperature of 500 °C. Figure 2 shows the XRD analysis of Cu<sub>2</sub>O/AC. For zinc, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O is reported to decompose to ZnO at > 200 °C [16], therefore it treated to 250 to get ZnO phase as shown in Figure 3. Finally, for nickel the oxidation phase was NiO when treated the impregnated AC at 500 °C because Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O is reported to converted to NiO when treated at temperature > 350 °C [17]. Figure 4 shows the XRD analysis of nickel- impregnated AC sample.

As shown in Figures 2, 3 and 4, the XRD patterns seems a noisy background, as generally noted for amorphous and unorganized carbon solid materials [18] and noted peaks representing crystalline zinc, copper and nickel species as ZnO/AC, Cu<sub>2</sub>O/AC, and NiO/AC respectively. For copper sample, diffraction peaks at 2θ = 36°, 42.5°, 61° and 74° indicate presence of Cu<sub>2</sub>O crystals in AC. For zinc sample diffraction peaks at 2θ = 36°, 47.5° and 74° indicate presence of ZnO crystals. The peaks spotted at 2θ = 37°, 62.7° and 75.4° are assigned to NiO particles for AC-NiO sample.

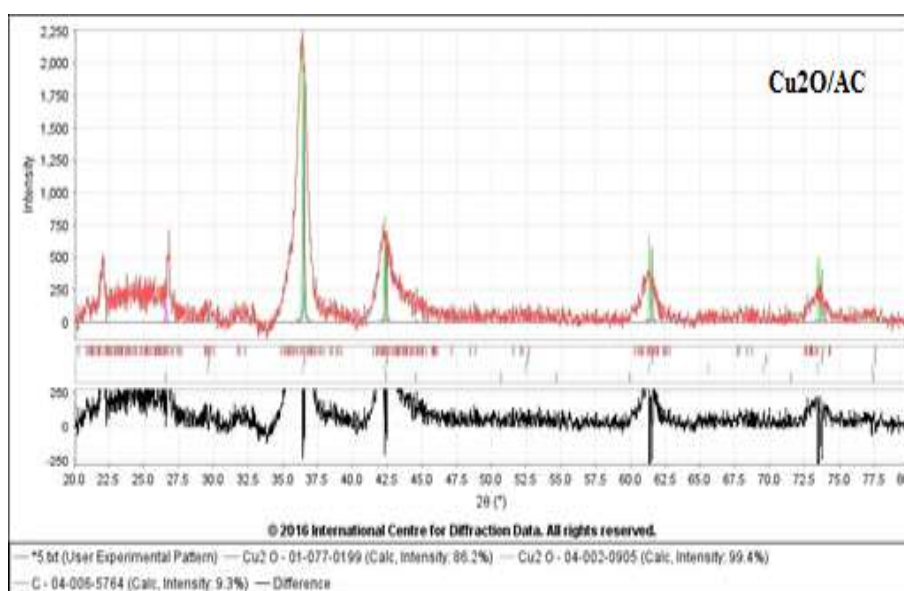


Figure 2: XRD analysis of Cu<sub>2</sub>O - impregnated AC adsorbent.

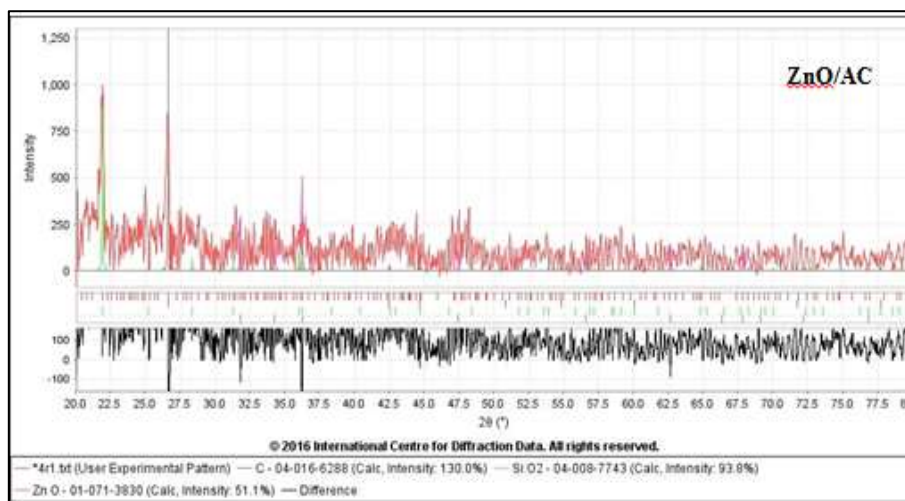


Figure 3: XRD analysis of ZnO - impregnated AC adsorbent.

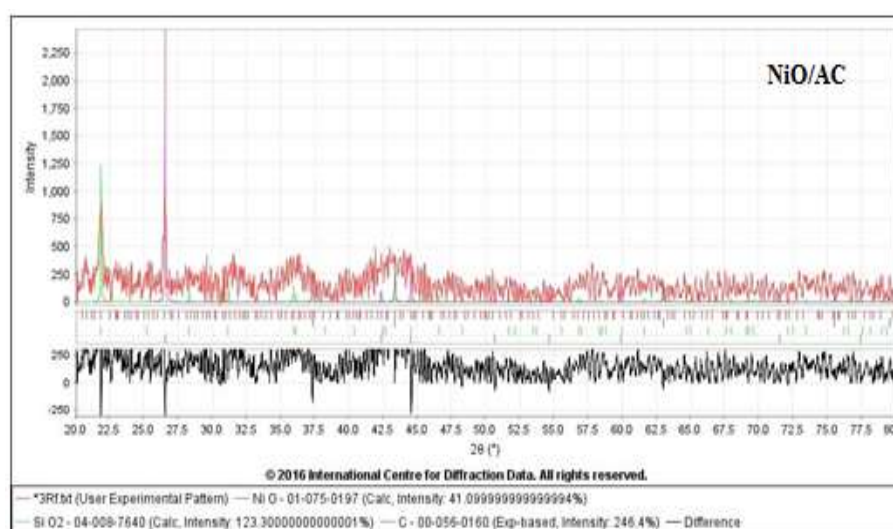


Figure 4: XRD analysis of NiO- impregnated AC sample.

The total content of metal of three samples impregnated with zinc, copper or nickel species onto AC were calculated in order to ensure if all zinc, copper, and nickel in their nitrate solution were deposited onto AC. The measured total content of zinc, copper and nickel were about 9.6, 11 and 10 wt% respectively which are close to the targeted 10% loading amount.

BET surface area and total pore volume of AC loaded with zinc, copper or nickel species are measured to estimate the effect of different metal impregnation on the porosity of the prepared adsorbents. All metal-impregnated samples have a surface area and total pore volume values almost comparable to those of original AC as shown in Table 3. The values in this Table indicate that the impregnating of 9.6, 9.25 and 8.7 wt.% of zinc, copper, and nickel on AC did not have a big effect on the porosity of produced adsorbent. Therefore, there are few carbon pores

plugged due to metal impregnation compared with the original AC.

Table 3: Surface area and pore volume of adsorbents.

Sample	BET surface area m <sup>2</sup> /g	Pore volume cm <sup>3</sup> /g
AC	1066	0.65
ZnO/AC	972	0.55
Cu <sub>2</sub> O/AC	995	0.592
NiO/AC	1046	0.578

## II. Desulfurization study

### 1) Batch study

In this study the adsorbent's concentration was varied as 0.01, 0.02, 0.04 and 0.08 g/ml. Figures 5 and 6 show the effect of adsorbent's concentration on the gasoil desulfurization (%) while Figure 7 shows adsorption capacity vs. equilibrium concentration for gasoil fuel adsorption on ZnO/AC, Cu<sub>2</sub>O/AC and NiO/AC (initial sulfur concentration of 990 and

equilibrium time of 5 hr). It is clear that the desulfurization yield (percent removal and adsorption uptake) increase with increasing adsorbent dose. This may be attributed to the larger surface area and therefore large active complexation sites, which are available for the sulfur compounds adsorption.

2) Continuous study

Continuous desulfurization of gasoil was carried out in fixed bed adsorber at room temperature, constant liquid hourly space velocity (LHSV) of  $3.5 \text{ hr}^{-1}$  and a bed height of 5 cm. Figure 8 shows the breakthrough curves for sulfur adsorption from gasoil fuel on ZnO/AC, Cu<sub>2</sub>O/AC, and NiO/AC adsorbent in term of ( $C_e/C_{in}$ ) vs. time. The time of breakthrough point was 4 hr for NiO/AC and 5 hr for both Cu<sub>2</sub>O/AC and ZnO/AC. This may have attributed to that the Cu<sub>2</sub>O/AC, ZnO/AC and NiO/AC has specific  $\pi$ -complexation and acid-base interactions between metal species and thiophene molecules in the order of Cu<sub>2</sub>O/AC > ZnO/AC > NiO/AC > AC.

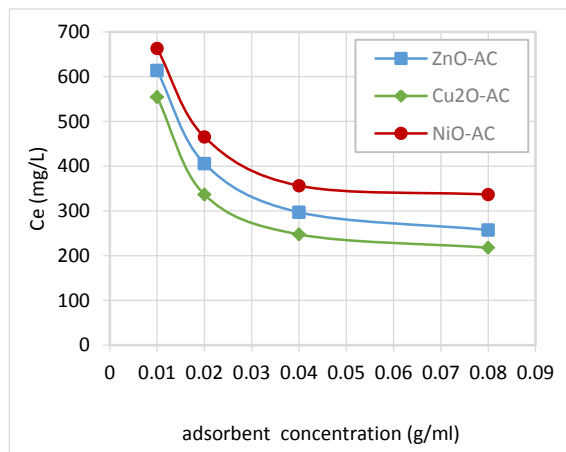


Figure 5: Effect of adsorbent's concentration on the equilibrium sulfur concentration,  $C_e$  for gasoil fuel (initial sulfur concentration: 990 ppm and equilibrium time of 5 hr).

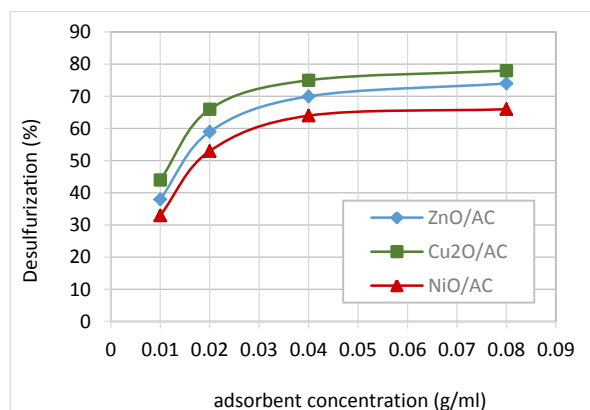


Figure 6: Effect of adsorbent's concentration on the desulfurization for gasoil fuel (initial sulfur concentration: 990 ppm and equilibrium time: 5 hr).

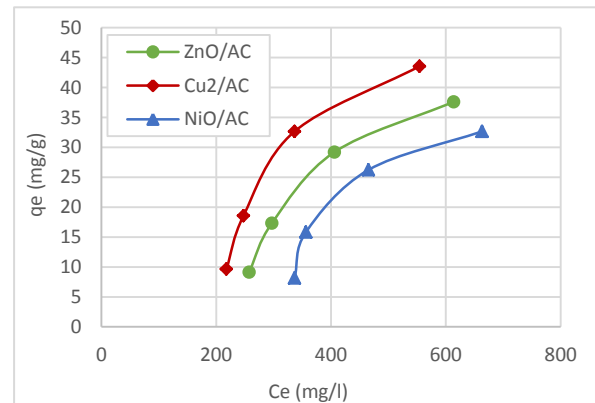


Figure 7: Adsorption capacity vs. equilibrium concentration of gasoil fuel (initial sulfur concentration: 990 ppm and equilibrium time: 5 hr).

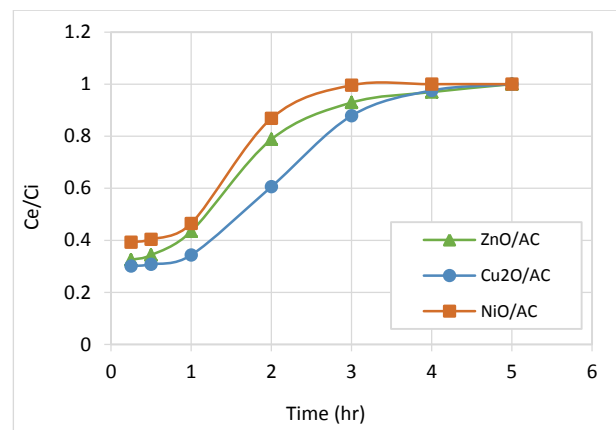


Figure 8: Experimental breakthrough curves for gasoil fuel desulfurization on different adsorbents (initial sulfur concentration: 990 ppm, liquid hourly space velocity:  $3.5 \text{ hr}^{-1}$  and a bed height: 5 cm).

4. Conclusion

Adsorptive desulfurization of Iraqi gasoil fuel in batch and column study was performed using three different adsorbents (ZnO/AC, Cu<sub>2</sub>O/AC, and NiO/AC) prepared by using impregnation method. The following conclusions can be summarized from the presented study:

- Using activated carbon in adsorptive desulfurization method for sulfur compounds removal from liquid fuels was very efficient especially when loaded with metal oxides. The experimental results indicate that the thiophenic compounds removal or uptake was enhanced when metals zinc, copper, and nickel were loaded onto activated carbon surface (between 15-37 %)

- Experimental results showed that copper oxide adsorbent was the most well prepared above zinc oxide and nickel oxide, it also showed a remarkable capability in sulfur removal from gasoil. In general, sulfur adsorption uptake of the three adsorbents followed the order of  $\text{Cu}_2\text{O}/\text{AC} \geq \text{ZnO}/\text{AC} > \text{NiO}/\text{AC}$ .
- In batch adsorption study, the only variable considered was changing the adsorbent concentration; results showed that optimum desulfurization achieved by the highest adsorbent's concentration and especially by  $\text{Cu}_2\text{O}$ , due to the highest surface area available for sulfur uptake, and thereby highest active sites offered by copper oxide adsorbent.
- In continuous adsorption, it dealt only with contact time parameter and at constant conditions of flow rate (LHSV) and bed height.  $\text{Cu}_2\text{O}/\text{AC}$  adsorbent offered an optimum desulfurization percentage for the most efficient active sites it possessed. The time of breakthrough point was 4 hr for  $\text{NiO}/\text{AC}$  and 5 hr for both  $\text{Cu}_2\text{O}/\text{AC}$  and  $\text{ZnO}/\text{AC}$ .

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