IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.15 No4 (December 2014) 25-35
ISSN: 1997-4884

University of Baghdad
College of Engineering

Removal of SO_2 over Modified Activated Carbon in Fixed Bed Reactor: I, Effect of Metal Oxide Loadings and Acid Treatment

Neran K. Ibraheem[1], **Shahrazad R. Raouf**[2], **Zainab A. Naser**[3*]
[1, 2, 3] Chemical Engineering Department, University of Technology, Baghdad, Iraq

Abstract

The removal of SO_2 from simulated gas stream (SO_2 + air) in a fixed bed reactor using Modified Activated Carbon (MAC) catalysts was investigated. All the experiments were conducted at atmospheric pressure, initial SO_2 concentration of 2500 ppm and bed temperature of 90^oC. MAC was prepared by loading a series of nickel and copper oxides 1, 3, 5, 7, and 10 wt% on AC. In some of the experimental runs, the original activated carbon was pretreated with two different concentrations of nitric acid 10 and 45 wt%. The results showed that the SO_2 removal efficiency, breakthrough time ($\tau_{0.05}$) and sorption capacity increase with increasing metal oxides loadings up to a value of 7 wt% beyond which the desulfurization performance decreases. The pretreatment of the original AC with HNO_3 enhanced the removal efficiency of SO_2. The copper supported catalysts showed higher flue gas desulfurization activity as compared to the nickel supported catalysts.

Keywords: SO_2 removal, Modified Activated Carbon, Acid Treatment, Fixed Bed Reactor, SO_2 Adsorption.

Introduction

Sulfur dioxide (SO_2) is one of the gravest chemical threats to the global environment and considered both primary and secondary pollutant [1, 2]. It emits to the atmosphere from power plants, industry, refining of petroleum, smelting of ores and manufacture of sulfuric acid as primary pollutant [3, 4]. Some industrial sources emit H_2S, which is oxidized to form H_2O and secondary pollutant SO_2, through the most important oxidizing reaction for H_2S with ozone [2]. The famous method for reducing emissions of SO_2 is flue gas desulfurization (FGD). A large number of FGD processes (regenerable and non-regenerable) have been developed and are expected to play an important role in reducing SO_2 emission from power plants [5]. The SO_2 removal by dry-regenerable methods provides an appropriate alternative to control the emissions of SO_2 from oil-fired power plants [6]. Being relatively simple and of low cost, dry adsorption with activated carbon (AC) or other adsorbents for SO_2 removal is being increasingly employed by most industries [7]. Pre-treatment of the AC or addition of promoters can significantly affect the dispersion of the active species [8, 9]. Wang and lu [10], examined the effects of acid treatments by HCL, HF and HNO_3 on the properties of Ni supported AC catalyst. It was found that acid treatment significantly changed the surface chemical properties and enhanced the surface area of the AC. It was believed that the HNO_3 as an oxidant can also oxidize some complexes producing acidic groups. The increase in surface acidity leads to more homogeneous distribution of nickel salt on AC. Tseng and Wey [11], found that the surface oxygen groups of the carbon support played a major role in determining the extent and strength of interaction with the metal precursor during catalyst preparation. The dispersion of supported metal is one of the main parameters related to its catalytic activity [12]. It is reported that the SO_2 adsorption characteristics of active carbons are strongly influenced by the presence of certain transition metal derivatives [13]. Some authors have reported that Ca^{+2} and Mo^{+2} ions had the greatest effect on the increase of SO_2 conversion [14]. It was established that heat treatment of modified AC (impregnated with aqueous solution of ($Ni(NO_3)_2.6H_2O$) up to 400°C leads to additional activation of the samples, which is accompanied by an increase in their adsorption characteristics (surface area). Destruction of the texture and decrease in the adsorption characteristics of the samples were observed at 550°C [15]. While, Jiaxiu et al. [16], found the characterization results showed that the Ni species on the catalyst (Ni/AC, Ni content of the catalyst was 0.92%) calcined at 400°C is Ni_2O_3. After calcination at 550°C, NiO species is formed on the AC. NiO and Ni coexist on the Ni/AC catalyst calcined at 800°C and only pure Ni species is observed after calcination at 1000 °C. This suggested that Ni can form different chemical states on the Ni/AC catalyst calcined at different temperatures, which can lead to a different desulfurization performance. Ni/AC catalysts containing only NiO or NiO and Ni coexisting together exhibit good catalytic activity at low reaction temperature 90 °C. Also, it was found that the V_2O_5 plays little role in SO_2 adsorption but a main role in the oxidation of SO_2 [17]. López et al. [18], found that the adsorption profiles of AC, demineralized activated carbon (DAC), treatment of AC with HCl-HF-HNO_3 solutions, and Cu supported DAC (Cu/DAC) show a similar behavior for adsorption of SO_2 but, for the Cu/DAC sample the SO_2 adsorption continues for more than 7h, which could indicate that there is a favorable effect of Cu which catalyzes the adsorption of SO_2 on the carbonaceous material, this increases the breakthrough time and the adsorption capacity.

The objective of the present study is to investigate the effect of the NiO and CuO loadings and the treatment of the original AC with nitric acid on the removal efficiency of SO_2 from simulated gas stream.

Experimental Work

Catalyst Preparation

The Modified Activated Carbon (MAC) was prepared by using industrial grade, granular activated carbon obtained from local markets, as a support. The chemical analysis (measured by atomic absorption technique), and the physical properties of the original AC (measured by automated surface area and porosity analyzer, (Micromeritics Company, USA)) are given in Tables 1 and 2 respectively. Prior to the impregnation process, AC was sieved to a size of 1 mm and dried in an oven at 110 °C for 4 hours, then it was impregnated with different concentrations of an aqueous solution of ($Ni(NO_3)_2.6H_2O$) to give nickel oxide supported AC with different loadings of 1, 3, 5, 7 and 10 wt%. The samples was dried at 110 ^oC in an oven for 4 hours and then calcined at 400 ^oC for 4 hours. These catalysts were labeled as 1Ni/AC, 3Ni/AC, 5Ni/AC, 7Ni/AC, and 10Ni/AC respectively. In some of the experimental runs, the original AC was pretreated with two different concentrations of nitric acid (10 and 45 wt%) and labeled as 10NAC and 45NAC respectively. Using the same method, copper oxide supported AC with different loadings of 1, 3, 5, 7 and 10 wt% were prepared by using an aqueous solution of ($Cu(NO_3)_2.6H_2O$) and labeled as 1Cu/AC, 3Cu/AC, 5Cu/AC, 7Cu/AC, and 10Cu/AC respectively. All the details of the required quantities of chemicals required to prepare the different NiO and CuO loadings supported AC catalysts are presented in table 3 and 4.

Table 1: Chemical Analysis of AC

Material	Wt %	Material	Wt %
C	92.46	Zn^{+2}	0.025
Ca^{+2}	2.75	Mg^{+2}	3.25
Co^{+2}	0.075	Mn^{+2}	0.1163
Cu^{+2}	0.15	Pb^{+2}	0.5125
Fe^{+2}	0.0696	PO_4^{-3}	0.0183
Fe^{+3}	0.325	SO_4^{-2}	0.0183
Others 0.23 *Wt%*			

Table 2: Physical Properties of AC

Test	Results
Surface area (m^2/g)	702
Pore volume (cm^3/g)	0.59
Bulk density (g/cm^3)	0.72
Particle density (g/cm^3)	1.91

Table 3: Details of Loadings NiO on AC

NiO (wt %)	Symbol	AC (g)	$Ni(NO_3)_2.6H_2O$ (g / 100 cm^3 H_2O)
1	1Ni/AC	95.05	4.95
3	3Ni/AC	85.14	14.86
5	5Ni/AC	75.23	24.77
7	7Ni/AC	65.32	34.68
10	10Ni/AC	50.45	49.55

Table 4: Details of Loadings CuO on AC

CuO (wt %)	Symbol	AC (g)	$Cu(NO_3)_2.3H_2O$ (g / 100 cm^3 H_2O)
1	1Cu/AC	96.19	3.8
3	3Cu/AC	88.6	11.40
5	5Cu/AC	80.99	19.01
7	7Cu/AC	73.39	26.61
10	10Cu/AC	61.99	38.01

Chemicals for SO_2 Generation and Detection

For the generation and detection of SO_2, Sodium sulfite, Na_2SO_3 was supplied from Merck, Germany. Sulfuric acid, H_2SO_4, iodine, I_2, Iodine ampoule, 0.1 N, potassium iodide, KI, starch and Sodium thiosulfate ampoule, 0.1 N were analytical grade reagents from BDH, England.

Experimental Rig

A schematic diagram of lab scale experimental rig designed for the adsorption of SO_2 from simulated gas stream (SO_2+Air) is shown in Figure 1. The rig consists of three sections: SO_2 generation section, sorption section and the analysis section. For the generation of SO_2, a three neck QVF 3 L-flask connected at its upper part to a glass burette 200 ml capacity which contains sulfuric acid was used. 2500 ppm of SO_2 was generated by dropping specified concentration of sulfuric acid solution into the SO_2 generation vessel that contained sodium sulfite. The inlet of the generation section is connected to a compressed air source. The test section is a QVF column, 2.54 cm inside diameter and 50 cm long, filled with catalyst to a height of 4 cm. The SO_2 removal was carried out at 90^oC, 1 bar and 140 ℓ/h gas flow rate. The rig was insulated with glass wool to maintain the test section temperature nearly constant. Calibrated rotameters were used to measure the gas flow rate. The initial and final weights of the catalyst were measured to determine the total amount of SO_2 adsorbed. The weight of SO_2 Adsorbed was determined by measuring the residual amount by its quantitative reaction with iodine and titrating excess iodine with sodium thiosulfate. The number of iodine equivalents is equal to the residual SO_2 in the trap of the analysis section.

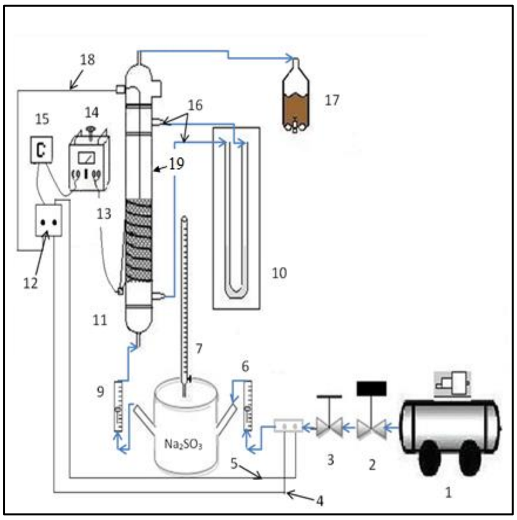

Fig. 1: Schematic Diagram of the Experimental Apparatus. (1) Compressor (2) Needle Valve (3) Regulator (4&5) Wet and dry bulb thermocouple (6) Rotameter1 (7) Burette (8) SO_2 generation vessel (9) Rotameter2 (10) U-tube manometer (11) Heater (12) Selector switch (13) AC (14) Variac (15) Temperature controller (16) Pressure drop (17) Absorption trap (18) Bed thermocouple (19) Reactor

Data Analysis

The total amount of SO_2 adsorbed (mg/g) was calculated as the ratio of the difference between the initial weight of the catalyst (fresh bed) and the final weight of the catalyst (spent bed) to the initial weight of the catalyst, as shown in Equation 1.

$$Sorption\ Capacity = \frac{W_f \;-\; W_S\ (mg)}{W_f\ \ (g)} \quad \ldots(1)$$

The removal efficiency of SO_2 was calculated as the ratio of SO_2 concentration that was removed by catalyst to the initial concentration of SO_2 gas fed to the bed, as in Equation 2.

$$\eta\,\% = \frac{C_o \;-\; C}{C_o} * 100 \qquad \ldots(2)$$

Full details of the experiment results and data analysis are given in [19].

Results and Discussion

Effect of Metal Loadings

The effect of nickel oxide loadings on SO_2 sorption capacity and the dynamic SO_2 removal efficiency before breakthrough point at gas rate of 140 ℓ/h, bed temperature of 90℃, and bed height of 4cm are shown in Figures 2 and 3 respectively. The results indicate that the nickel oxide supported AC can significantly improve the desulfurization efficiency of the original AC. Figures 4 and 5 show the relation between the breakthrough time ($\tau_{0.05}$) and the sorption capacity with Ni/AC loadings respectively. It can be noticed from these figures that the breakthrough time and the SO_2 sorption capacity increase as the Ni loading increases up to a value of 7 wt% beyond which the desulfurization performance decreases. For 7 wt% loaded AC, the breakthrough time and the sorption capacity increased to 165 minutes and 191 mg/g respectively as compared to 38 minutes and 120 mg/g for the original AC. 7Ni/AC catalyst exhibited the highest desulfurization activity, this behavior may be attributed to the uniform distribution of the active phase within the support and to the type and degree of interaction reached during the impregnation process. The decrease in desulfurization performance beyond 7 wt% Ni may be ascribed to the intimate interaction between nickel nitrate and AC in impregnation step which leads to the occlusion of small amounts of AC in Ni derivatives crystallites upon calcination [20].

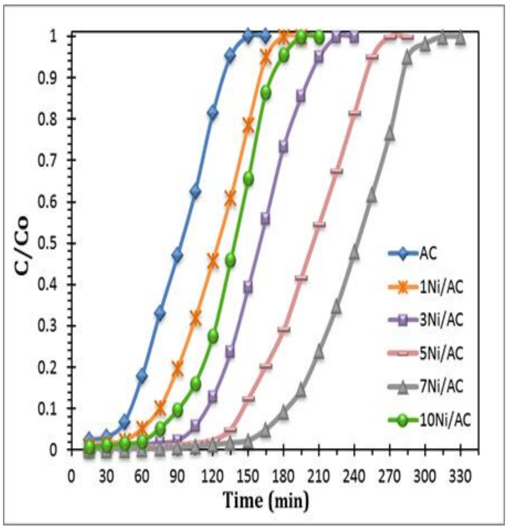

Fig. 2: Effect of NiO Loadings on SO_2 Sorption Breakthrough

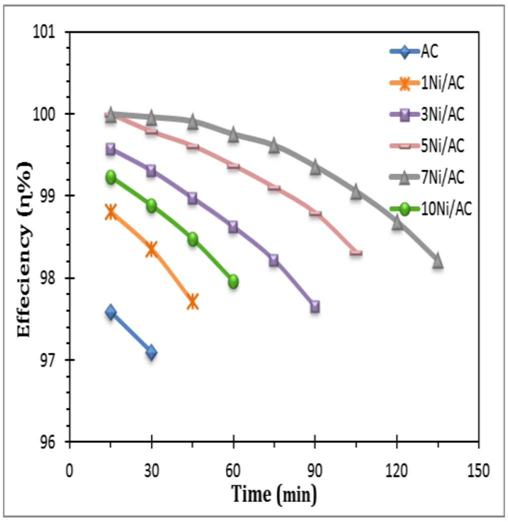

Fig. 3: Dynamic Change of SO_2 Removal Efficiency for Different NiO Loadings

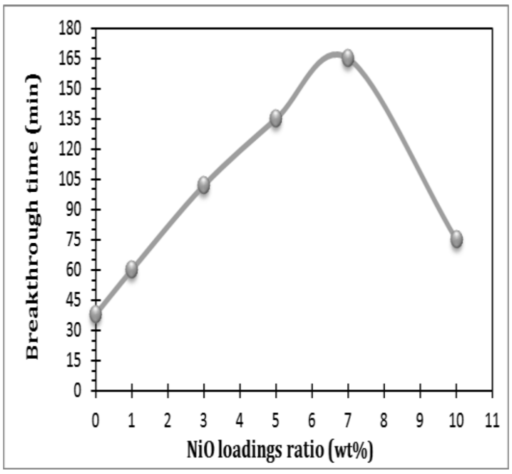

Fig. 4: Effect of Ni O Loadings on Breakthrough Time

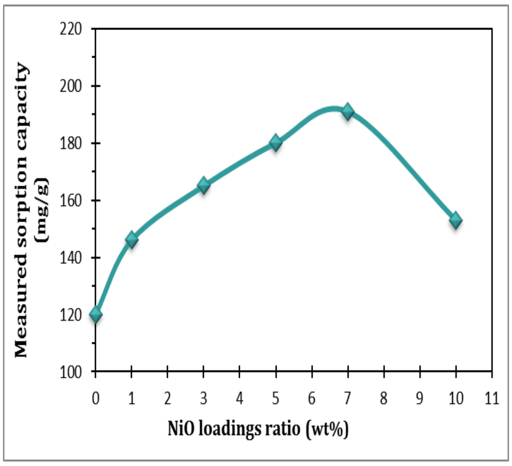

Fig. 5: Sorption Capacity of SO_2 for Different NiO Loadings

Effect of Acid Treatment

The breakthrough curves and the dynamic SO_2 removal efficiency of 7Ni/AC and 7Ni/NAC catalysts are presented in Figures 6 and 7 respectively. The results indicate that the acid treatment significantly enhanced the SO_2 removal efficiency, the desulfurization activity of the catalysts is in the following sequence from poor to excellent: 7Ni/AC<7Ni/10NAC< 7Ni/45NAC, indicating that the increase in concentration of acid treatment results in a more homogeneous distribution of nickel oxide on AC and increase the surface area of catalyst.Surface oxygen on carbon consists of inorganic and Organic matters. Acid treatment mainly removes the inorganic oxides and increases the organic oxygen-containing materials, this removal leaves sites on the carbon surface which can chemisorb oxygen in air and this would result in more oxygen surface complexes which are more acidic [21]. The results that are presented in precedent figures are in agreement with the result obtained by Leon and Radovic [22], and Tseng et al. [23] who proposed that the interaction between metallic precursor and carbon support depends on the amphoteric character of carbon material. At pH > pH_{slurry} the acidic groups on the carbon surface will dissociate; the negatively charged surface then attracts and adsorbs cations from the solution; at pH < pH $_{slurry}$ it will attract anions. In other words, if the pH of the impregnation solution is higher than the pH of the aqueous slurry of the support (pH_{slurry}), then the adsorption of cations is favored. In this sense, these surface oxygen groups can be considered as the anchoring centers for the metal precursor and its presence should favor higher dispersions.

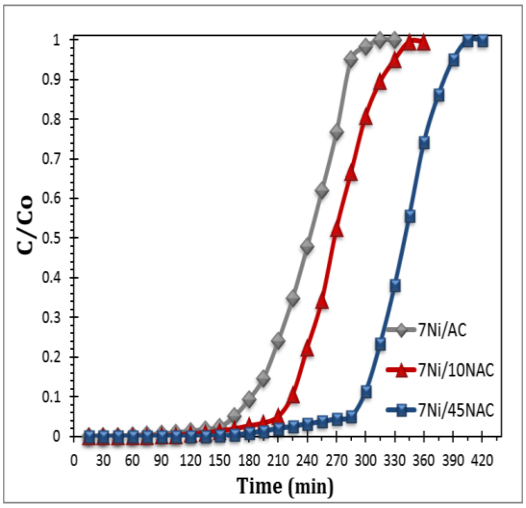

Fig. 6: Dynamic Change in SO_2 effluent concentration for 7Ni/NAC Catalysts

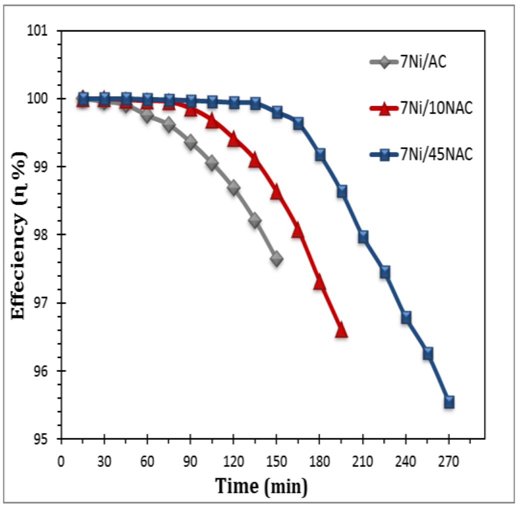

Fig. 7: Effect of HNO_3 Concentration on SO_2 Breakthrough time for 7Ni/NAC Catalysts

Figures 8 and 9 indicate that as the acidity of the AC increased the breakthrough time and the sorption capacity increased. The breakthrough time increased from 210 minutes to 285 minutes and the sorption capacity increased from 197 mg/g to 208 mg/g as the concentration of HNO_3 increased from 10 to 45% for 7Ni/NAC catalyst. This may be attributed to the increase in surface area as given in Table 5. The results also indicate that the surface area of 7Ni/45NAC is lower than that of 45NAC this is mainly due to metal loadings. The better performance of 7Ni/45NAC as compared to 45NAC may be due to the role of Ni derivatives on catalytic activity.

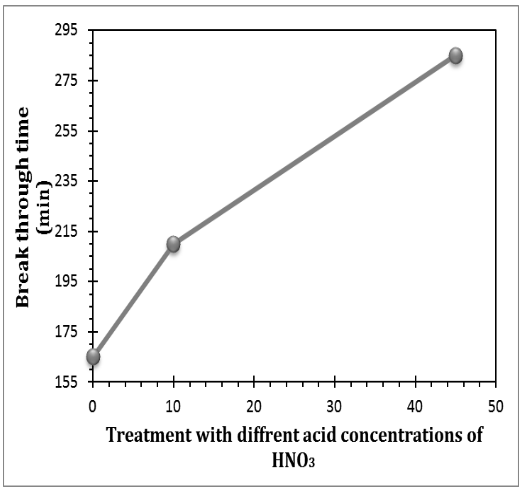

Fig. 8: Effect of HNO_3 Concentration on Breakthrough Time for 7Ni/NAC Catalyst

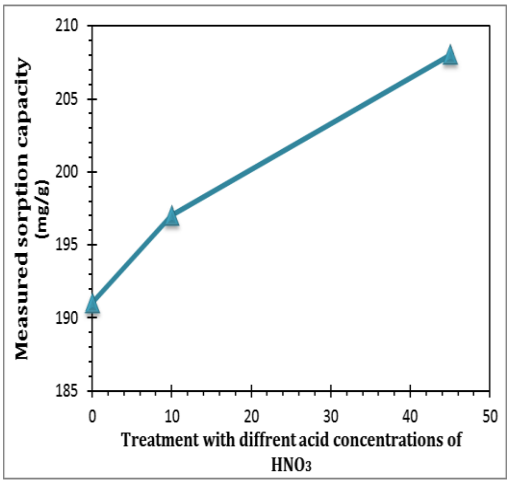

Fig. 9: SO_2 Sorption Capacity for Different HNO_3 Concentration for 7Ni/NAC Catalyst

Table 5: Surface Area (m^2/g) of AC Before and After Acid Treatment

Sample	Surface area
AC	702
10NAC	816
45NAC	1010
7Ni/10NAC	767
7Ni/45NAC	895

Acidic oxygenated surface groups (carboxylic, lactone, carbonyle, phenolic) were determined by Fourier transform infrared (FTIR, Bruker Company), the results are shown in Figures 10-13.

Lisovskii et al. [24] clarified that the carbon which contains more oxygenated groups and in which the acidity is higher, is characterized by a larger SO_2 adsorption. This indicates that there is an interaction between the SO_2 and the acidic oxygenated surface groups produced during oxidation and the presence of acid groups improved the extractability of the acid. Such oxygenated structures are also responsible for catalytic activity of carbon in SO_2 oxidation.

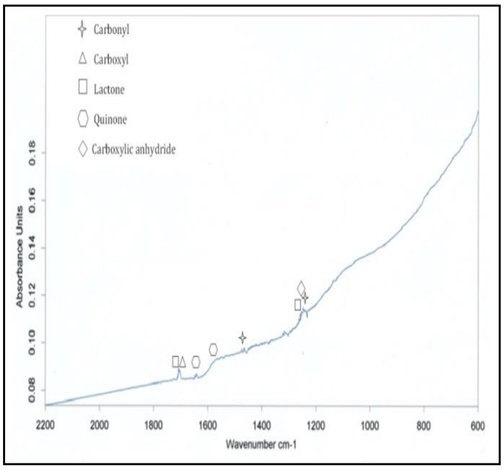

Fig. 10: FTIR Spectra of 7Ni/AC Catalyst in the 600-2200 cm^{-1} region

The chemical state of 7Ni/45NAC was characterized using X-ray Diffraction (XRD, Shimadzu Company) and the crystalline phases were identified by comparison with reference data, International Center for Diffraction Data, (ICDD). The results as shown in Figure 14 indicate that NiO phase shows major peaks but minor Ni, $Ni(OH)_2$ and Ni_2O_3 peaks are detected.

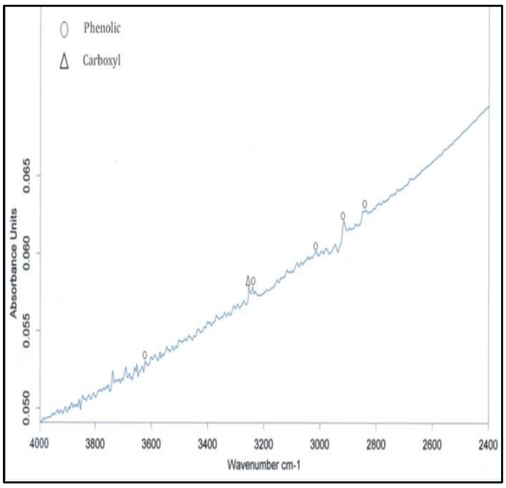

Fig. 11: FTIR Spectra of 7Ni/AC Catalyst in the 2400-4000 cm^{-1}region

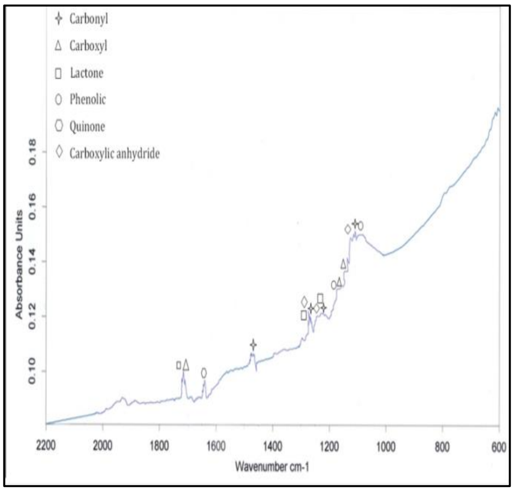

Fig. 12: FTIR Spectra of 7Ni/45NAC catalyst in the 600-2200 cm^{-1} region

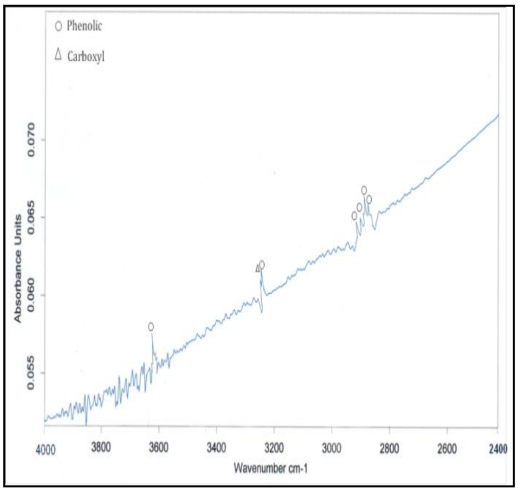

Fig. 13: FTIR Spectra of 7Ni/45NAC catalyst in the 2400-4000 cm^{-1} region

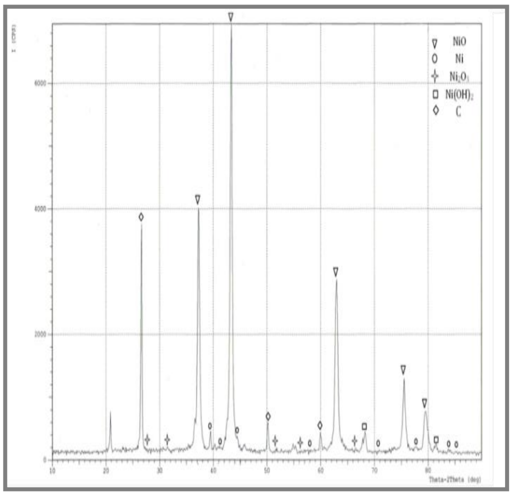

Fig. 14: XRD Patterns of 7Ni/45NAC

This is attributed to that all the catalysts were calcined at 400 °C, and Ni is rarely formed at this temperature [15]. The coexistence of Ni and NiO species on the activated carbon favors the flue gas desulfurization.

Comparison between the Performance of NiO and CuO Supported AC Catalysts

The desulfurization performance of Cu/AC catalysts is shown in Figures 15-18. Compared with AC, Cu/AC catalysts exhibit better performance. The SO_2 effluent concentration decreased from 60 ppm to zero ppm and the SO_2 removal efficiency increased from 97.5% to 100% at time duration of 15 minutes. This may be expected due to modifications of physical and chemical properties of AC. The same behavior was obtained by other investigators [14, 25, 26]. The change in sorption breakthrough and removal efficiency with time for different CuO loadings is shown in Figures 15 and 16. The results indicate that the removal efficiency increases as the metal loading increases. This behavior is to be expected due to that low loading offer few active sites of Cu and thus show lower activity; higher loading above 7wt% resulted in active sites aggregation and consequent reduction of catalytic activity. Similar behavior was also obtained with Ni/AC catalysts. The breakthrough time and sorption capacity of Cu/AC were higher than those of Ni/AC. The breakthrough time ($\tau_{0.05}$) for 7Cu/AC compared to 7Ni/AC increased from 3h to 4h and the sorption capacity increased from 191 mg/g to 200 mg/g as shown in Figures 17 and 18. This may be attributed to that Cu and its derivatives favoring more transformation of the adsorbed SO_2 and oxidizing SO_2 into other more stable SO_3 and H_2SO_4. The present findings are in agreement with the results obtained by Tseng et al. [25] and López et al. [18] but differ from Ma et al. [17] who showed that metals play little role in SO_2 adsorption but a main role in oxidation of SO_2.

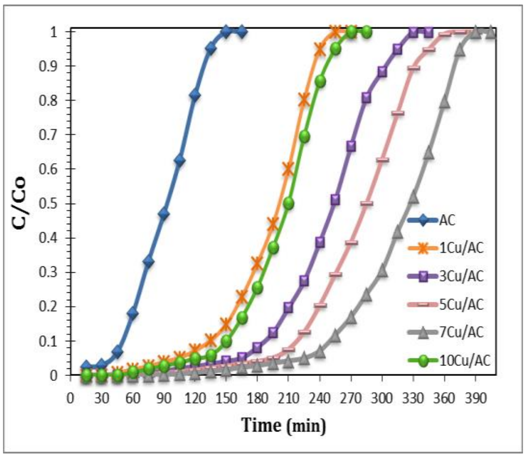

Fig. 15: Effect of CuO Loadings on SO_2 Sorption Breakthrough

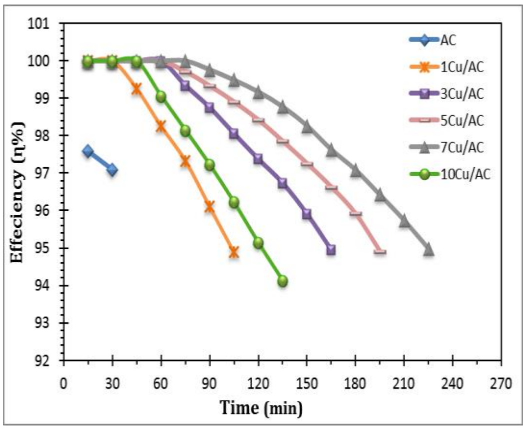

Fig. 16: Dynamic Change in SO_2 Removal Efficiency for Different Copper Oxide Loadings

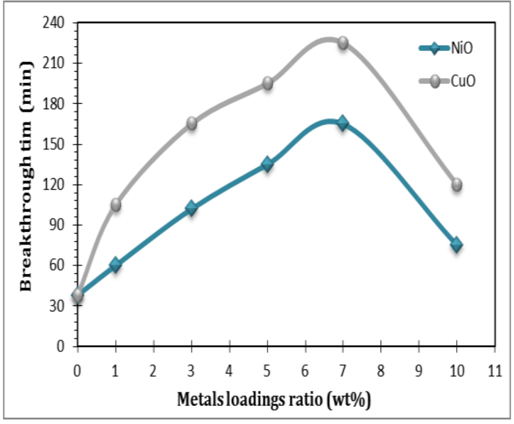

Fig. 17: Breakthrough Time of Ni/AC and Cu/AC Catalysts with Different Metal Loadings

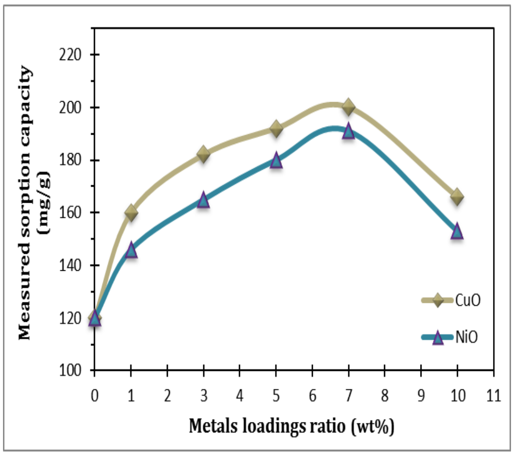

Fig. 18: Sorption Capacity of Ni/AC and Cu/AC Catalysts with Different Metal Loadings

Conclusions

1. For both nickel and copper Oxides supported AC catalysts, 7wt% metal loading gave the optimum desulfurization efficiency, sorption capacity and breakthrough time.
2. The chemical state of the 7Ni/45NAC catalyst as characterized using XRD, shows major peaks for NiO phase but minor Ni, $Ni(OH)_2$ and Ni_2O_3 peaks were detected.
3. Fourier Transform Infra-Red (FTIR) and surface area tests showed that the oxygen containing functional groups and the surface area of AC increase with increasing the concentration of nitric acid.
4. Compared with nickel supported AC catalysts, the copper supported AC catalysts showed similar behavior in SO_2 removal. However the breakthrough time and sorption capacity of Cu/AC catalysts were higher than those for Ni/AC. The breakthrough time and sorption capacity for 7Cu/AC were 4hours and 200mg/g as compared to 3hours and 191mg/g for Ni/AC respectively.

Notation

Symbol	Description	Unit
C	Exit SO_2 Concentration	ppm
Co	Initial SO_2 Concentration	ppm
W_f	Mass of fresh catalyst	g
W_s	Mass of spent catalyst	g
$\tau_{0.05}$	Breakthrough time	min
AC	Activated Carbon	--
MAC	Modified Activated Carbon	--

References

1- Lee, K., T., Christopher, K., C., Fernando, W., J., Bhatia, S., and Mahamed, A., "**Modeling and Simulation of Flue Gas Desulfurization Using CaO/Coal Fly Ash Sorbent**", *J. of Chem. Eng. Of Japan*, Vol. (38), No.(6), PP. (391-396), (2005).

2- Davis, M., L., and Cornwell, D., A., "**Introduction to Environmental Engineering**", 4th Ed., McGraw-Hill, USA, (2008).

3- Sander, V., H., Fisher, H., Rothe, U., and Kola, R., "**Sulphur, Sulphur Dioxide and Sulphuric Acid**", 4thEd., the British Sulphur Coporation Ltd, London, (1984).

4- Irvan, **"Removal of SO_2 and NO from Simulated Flue Gas Using Rice Husk Ash/CaO/CeO_2 sorbent"**, PhD Thesis, University Sains, Malaysia, (2009).

5- Hanski, T., **"Feasibility of Dry Scrubbers for Ships and Stationary Diesel Power Plants"**, M.Sc. Thesis, University of Oulu, Finland, (2011).

6- Kohl, A., L., and Riesenfeld, F., C., **"Gas Purification"**, 3rd Ed., Houston, Texas, (1979).

7- Lua, A., C., and Gou, J., **"Adsorption of Sulfur Dioxide on Oil-Palm-Shell Activated Carbon in a Packed Bed"**, *Sustainable Energy and Environmental Technologies*, pp. (430-434), (2000).

8- De Miguel., S., R., Heinen, J., C., Castro, A., A., and Scelza, O., A., **"Effect of Acid Treatment on the Properties of an Activated Carbon"**, *React Kinet Catal Lett*, Vol. (40), No. (2), pp. (331–335), (1989).

9- Nakamura, T., Yamada, M., and Yamaguchi, T., **"Catalytic Properties of $Mo(CO)_6$ Supported on Activated Carbon for Ethene Homologation"**. *Appl Catal*, Vol. (87), No. (1), pp. (69–79), (1992).

10- Wang, S., and Lu, G., Q., **"Effects of Acidic Treatments on the Power and Surface Properties of Ni Catalyst Supported on Activated Carbon"**, *Carbon*, Vol. 36, No. (3), pp. (283-292), (1998).

11- Tesng, H., H., and Wey, M., Y., **"Effects of Acid Treatments of Activated Carbon on its Physiochemical Structure as a Support for Copper Oxide in $DeSO_2$ Recation Catalysts"**, *Chemosphere*, Vol. 62, No. (5), pp. (756-766), (2006).

12- Wang, S., B., and Lu, G., Q., **"Effects of Acidic Treatments on the Pore and Surface Properties of Ni Catalyst Supported on Activated Carbon"**, *Carbon*, Vol. (36), No. (3), pp. (283 – 292), (1998).

13- Klinik, J., and Grzybek, T., **"The Influence of Cobalt, Nickel, Manfanese and Vanadium to Active Carbons on their Efficiency in SO_2 Removal from Stack Gases"**, *Fuel*, Vol. (71), No. (1), pp. (1303-1308), (1992).

14- Martyniuk, H., and Więckowska, J., **"Adsorbents and Catalysts from Brown Coal for Flue Gas Desulfurization"**, *Fuel*, Vol. (74), No. (11), pp.(1716-1718), (1995).

15- Bekyarova, E., and Mehandjiev, D., **"Studies of Ni-Impregnated Active Carbon"**, *J. of Colloid and Interface Science*, Vol. (179), No. (0243), pp.(509-516), (1996).

16- Jiaxiu, G., Juan, L., Yinghao, C., Huaqiang, Y., and Yaoqiang, C., **"Influence of Ni Species of Ni/AC Catalyst on Its Desulfurization Performance at Low Temperature"**, *Chin. J. Catal.*, Vol. 31, No. (3), pp. (278-282), (2010).

17- Ma, J., Liu, Z., Liu, Q., Guo, S., Huang, Z., and Xiao,Y., **"SO_2 and NO Removal from Flue Gas over V_2O_5/AC at Lower Temperatures-Role of V_2O_5 on SO_2 Removal"**, *Fuel processing Technology*, Vol. (89), No. (3), pp.(242-248), (2008).

18- López, D., Buitrago, R., Escribano, A., Reinoso, F., and Mondragon, F.," **Low Temperature Catalytic Adsorption of SO_2 on Activated Carbon"**, *J. Phys. Chem. C*, Vol. (112), No. (39), pp. (15335-15340), (2008).

19- Nasir, Z., A., **"The Removal of SO_2 Over Modified Activated Carbon Catalyst in Fixed Bed Reactor"**, M.Sc. Thesis, University of Technology, Chemical Engineering, Iraq, (2012).

20- Richardson, J., T., **"Principle of Catalyst Development"**, Plenum press New York, pp. (288), (1989).

21- Wang, S., and Lu, G., Q., **"Effects of Acidic Treatments on the Power and Surface Properties of Ni Catalyst Supported on Activated Carbon"**, *Carbon*, Vol. (36), No. (3), pp. (283-292), (1998).

22- Leon y., Leon, C.A. and Radovic, L.R., **"Interfacial Chemistry and Electrochemistry of Carbon Surfaces"**, *Chemistry and Physics of Carbon*, Vol. (24), No. (2), pp. (213-310), (1994).

23- Tesng, H., H., and Wey, M., Y., **"Effects of Acid Treatments of Activated Carbon on its Physiochemical Structure as a Support for Copper Oxide in DeSO$_2$ Recation Catalysts"**, *Chemosphere*, Vol. (62), No. (5), pp. (756-766), (2006).

24- Lisovskii, A., Semiat, R., and Aharoni, C., **"Adsorption of Sulfur Dioxide by Active Carbon Treated by Nitric Acid: I. Effect of the Treatment on Adsorption of SO$_2$ and Extractability of the Acid Formed"**, *Carbon*, Vol. (35), No.(10-11), pp. (1639-1643), (1997).

25- Tesng, H., H., Wey, M., Y., and Fu, C., H., **"Carbon Materials as Catalyst Supports for SO$_2$ Oxidation: Catalytic Activity of CuO-AC"**, *Carbon*, Vol. (41), No. (1), pp. (139-149), (2003).

26- Sumathi, S., Bhatia, S., Lee, K., T., and Mohamed, A., R., **"Cerium Impregnated Palm Shell Activated Carbon (Ce/PSAC) Sorbent for Simultaneous Removal of SO$_2$ and NO-Process Study"**, *J. of Chemical Engineering*, Vol. (162), No. (5), pp. (51-57), (2010).