

Removal of SO₂ over Modified Activated Carbon in Fixed Bed Reactor: II.Effect of Process Variables on the Characteristics of Mass Transfer Zone

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ABSTRACT

Adsorption of sulfur dioxide (SO₂) onto NiO supported activated carbon (Ni/AC) in fixed bed reactor under different operating conditions was studied. Using 7Ni/AC catalyst, the effect of two process variables: namely gas flow rate ($80 \leq Q \leq 290$ l/h equivalent to superficial gas velocity $263 \leq V_g \leq 955$ cm/min) and bed height ($4 \leq H \leq 8$) cm on the desulfurization activity and the characteristics of mass transfer zone (MTZ) were investigated. Breakthrough curves for SO₂ under various adsorption conditions were obtained and some characteristic parameters such as breakthrough time ($\tau_{0.05}$), exhaustion time ($\tau_{0.95}$) and length of mass transfer zone (L_{MTZ}) were derived from these breakthrough curves. The experimental results revealed that on increasing gas rate for all bed heights two regions are developed.

Keywords: SO₂ Removal, Ni Supported Activated Carbon, Fixed Bed Reactor, Breakthrough curves, Mass Transfer Zone

إزالة غاز ثنائي اوكسيد الكبريت في مفاعل الطبقة الثابتة باستخدام الكاربون المنشط
المطور: 2- تأثير المتغيرات التشغيلية على خصائص منطقة انتقال الكتلة

الخلاصة

تم في هذا البحث دراسة إمتزاز غاز ثنائي اوكسيد الكبريت على الكاربون المنشط المحمل باوكسيد النيكل في مفاعل الطبقة الثابتة تحت ظروف تشغيلية مختلفة.

الكاربون المنشط المحمل بـ(7Ni/AC) من اوكسيد النيكل تم دراسة تأثير متغيرين تشغيليين هما : معدل تدفق الغاز (80-290) لتر/ساعة المكافئ الى سرعة الغاز (263-955) سم/دقيقة (وارتفاع الحشوة (4-12) سم على فعالية إزالة غاز ثنائي اوكسيد الكبريت وخصائص منطقة إنتقال الكتلة (MTZ).

تم الحصول على منحنيات إختراق غاز ثنائي اوكسيد الكبريت (Breakthrough curves) تحت ظروف إمتزاز مختلفة وبعض المعايير المميزة مثل زمن الإختراق ($\tau_{0.05}$ Breakthrough time) , زمن النفاذ ($\tau_{0.95}$ Exhaustion time) وطول منطقة انتقال الكتلة (L_{MTZ}) التي استمدت من هذه المنحنيات . أظهرت النتائج العملية ظهور منطقتين بزيادة معدل تدفق الغاز لجميع إرتفاعات الحشوة.

INTRODUCTION

Sulfur dioxide (SO₂) is a pollutant gas produced by various human activities such as the operation of industrial boilers and the burning of fossil fuel at power plants. Stringent environmental regulations limiting atmospheric SO_x emissions encourage the research to improve the current technology of flue gas desulfurization (FGD) and developed novel FGD technologies with resourceful utilization, low costs and high efficiency [1,2]. Activated carbons (ACs) are industrially applied in many processes either as catalyst or as adsorbent. Among these processes, carbon based flue gas cleaning attracts worldwide interest[3]. An enhancement of the AC's activity is required through a proper modification of the carbon characteristics and use of additives [4].The chemical nature of the active carbon surface, including acidic-basic properties, changes as a result of oxidation and high temperature treatment. Thus, after oxidation by nitric acid the amount of oxygen at the surface of the carbons increases with appearance of different oxygenated groups [5].Using AC as catalyst support offers several advantages because it is a relatively inexpensive, possess a complex porous structure and various surface functional groups which can be modified by physical or chemical treatments [6] and affect the characteristics of the catalyst[7]. Considering these facts, activated carbon may serve as a good support for SO₂ removal catalysts[8].The presence of certain transition group metals can favor the SO₂ adsorption on carbon[9]. Davini[10] found that iron appears to have a high activity in the global process of SO₂ fixation on the carbonaceous matrices and in its subsequent transformation into more stable compounds. In our previous work on SO₂ removal from flue gases using modified activated carbon catalyst, a series of NiO supported activated carbon catalysts was investigated. It was found that 7wt% NiO supported activated carbon with the original activated carbon being treated by nitric acid gave the highest SO₂ removal efficiency[11].The present paper reports continuation of the previous work. Breakthrough curves for SO₂ under various adsorption conditions were obtained and some characteristic parameters such as breakthrough time, exhaustion time and length of mass transfer zone were investigated.

EXPERIMENTAL WORK

Catalyst preparation

Using impregnation method 7wt% NiO supported activated carbon (AC) was prepared. Industrial grade granular activated carbon was used 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 an aqueous solution of (Ni(NO₃)₂.6H₂O) containing 34.68 g of salt per 100 ml of distilled water to obtain around 7 wt% NiO. During the impregnation, the solution of nickel nitrate was continuously mixed with AC by shaking for 20 minutes. The sample was then heated to about 50°C for 5h and dried at 110°C for 4h and calcined at 400°C for 4h[12, 13]. All the impregnation process was applied under condition of evacuation, this catalyst is labeled as 7Ni/AC. In some of the experimental runs, the original AC was

pretreated with two different concentrations of nitric acid (10 and 45wt%) and labeled as 10NAC and 45NAC respectively.

Table (1) Chemical analysis of AC.

Material	Wt %	Material	Wt %
C	92.46	Mg ⁺²	3.25
Ca ⁺²	2.75	Mn ⁺²	0.1163
Co ⁺²	0.075	Pb ⁺²	0.5125
Cu ⁺²	0.15	PO ₄ ⁻³	0.0183
Fe ⁺²	0.0696	SO ₄ ⁻²	0.0183
Fe ⁺³	0.325	Zn ⁺²	0.025
Others		0.23	

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

Experimental rig

The experiments were performed in a laboratory scale fixed bed reactor. A schematic diagram of the rig is shown in Figure (1). The rig consists of three sections: SO₂ generation section, test section and the analysis section. For the generation of SO₂ a three neck QVF3L-flask, connected at its upper part to a glass burette (200ml) capacity which contains sulfuric acid was used. 2500 ppm of SO₂ was generated by dropping the specified concentration of sulfuric Acid solution into the SO₂ 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, 2.54cm inside diameter and 50cm long. The required amount of sorbent supported by borosilicate glass wool was packed in the center of the reactor. The reactor was heated up to 90°C by external wired heater and the bed temperature was continuously monitored by a thermocouple.

Air stream, used as carrier gas, was mixed with SO₂ gas stream and fed to the reactor. The concentration of SO₂ 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 SO₂ in the trap of the analysis section[14]. The weight of SO₂ 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 SO₂ in the trap of the analysis section. The gas flow rate and bed heights were changed from 80-290 l/h and 4-8cm respectively. All the experimental runs were performed at 90°C and atmospheric pressure.

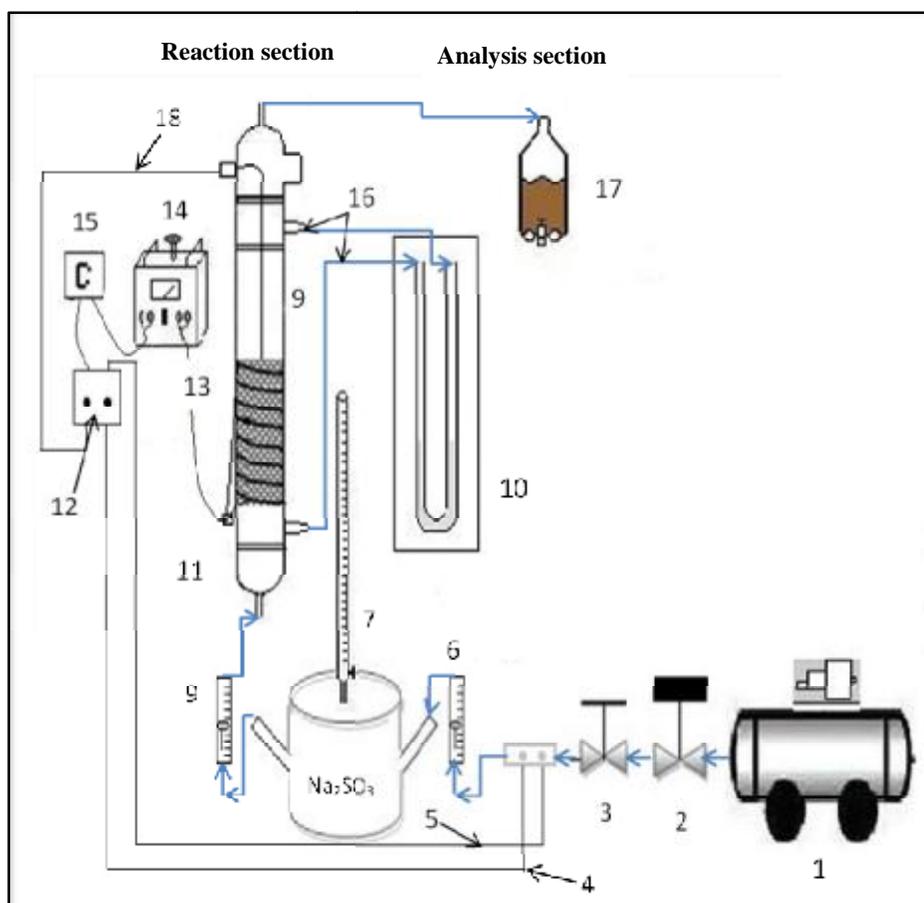


Figure (1): Schematic Diagram of the Experimental Apparatus. (1) Compressor (2) Needle Valve (3) Regulator (4&5) Wet and dry bulb thermocouple (6) Rotameter (7) Burette (8) SO₂ generation vessel (9) Rotameter (10) U-tube manometer (11) Heater (12) Selector switch (13) AC (14) Variac (15) Temperature controller (16) Pressure drop (17) Absorption trap (18) Bed thermocouple (19) Reactor.

THEORETICAL ANALYSIS**Removal Efficiency of SO₂ ($\eta\%$)**

The removal efficiency of SO₂ was calculated as the ratio of SO₂ concentration that was removed by catalyst to the initial concentration of SO₂ gas fed to the bed as shown in equation (1):

$$\eta\% = \frac{C_o - C}{C_o} * 100 \quad \dots (1)$$

Length of mass transfer zone (L_{MTZ})

The length of the mass transfer zone (L_{MTZ}) may be estimated as follows in equation (2)[15]:

$$L_{MTZ} = \frac{\tau_{0.95} - \tau_{0.05}}{(\tau_{0.95} + \tau_{0.05}) / 2} * L \quad \dots (2)$$

Where, L is the length of the packed bed (cm), $\tau_{0.05}$ and $\tau_{0.95}$ are the breakthrough and exhaustion time (min) respectively, which are normally defined as the times when the outlet concentrations are 5% and 95% of the inlet concentration respectively.

RESULTS AND DISCUSSION**Effect of Gas Rate**

Figures (2) to (7) show breakthrough curves and removal efficiency of SO₂ using 7Ni/AC at different gas rates and for different bed heights. The results indicate that for all bed heights a similar behavior is obtained. As the gas flow rate increases the SO₂ effluent concentration and breakthrough time decrease and the SO₂ removal efficiency increases to a point beyond which any further increase in the gas flow rate results in an increase in the SO₂ effluent concentration and breakthrough time, and decreases the SO₂ removal efficiency.

The optimum values of flue gas flow rates can be observed at 140, 230 and 260 l/h for bed heights of 4, 8 and 12 cm, respectively. The superficial velocity is proportional to the gas volumetric flow rate as the column cross-sectional area is constant in all the experimental runs.

At low flue gas flow rates, gas has less power; so long time is required to pass the mass transfer boundary layer thickness. By increasing the gas rate, the gas has enough power and time to diffuse across the boundary layer (diffusion control). At higher flue gas flow rates gas hasn't the sufficient time for the oxidation of large amount of SO₂ to form SO₃ which leads to the decrease in SO₂ Retention (reaction control). The same dependence on gas flow rates was also found in other packed-bed adsorption tests, Liu et al. [16], Li et al. [17] and Jawad [18].

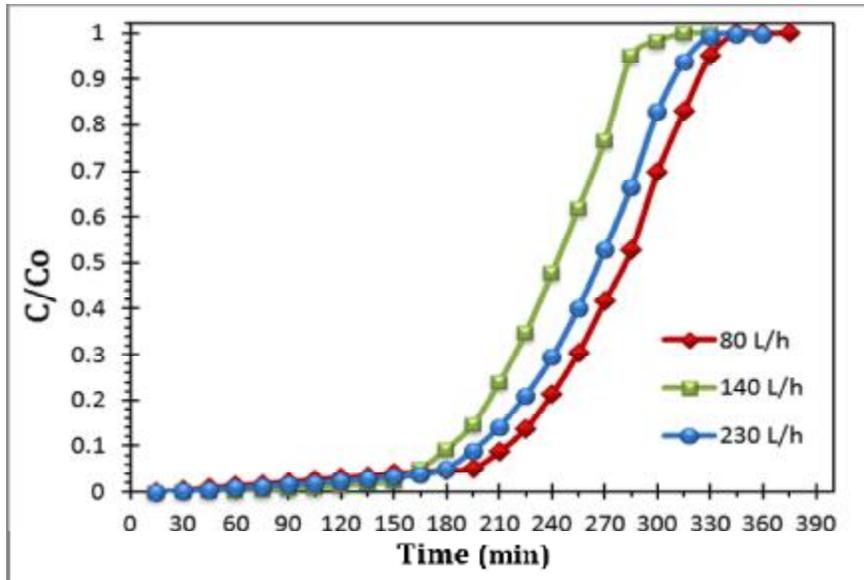


Figure (2): Breakthrough Curves of 7Ni/AC Catalyst with Different Flue Gas Flow Rates at Bed Height of 4cm.

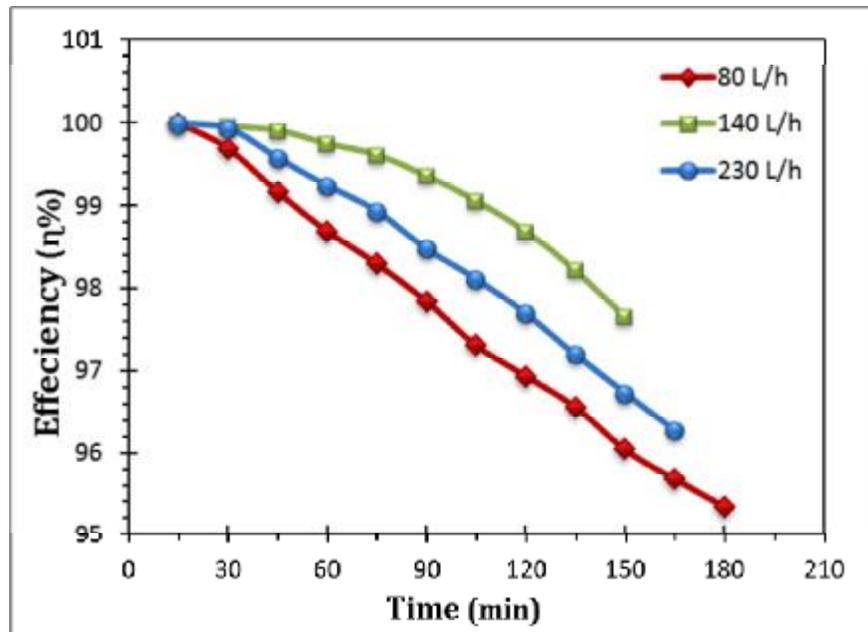


Figure (3): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Flue Gas Flow Rates at Bed Height of 4cm.

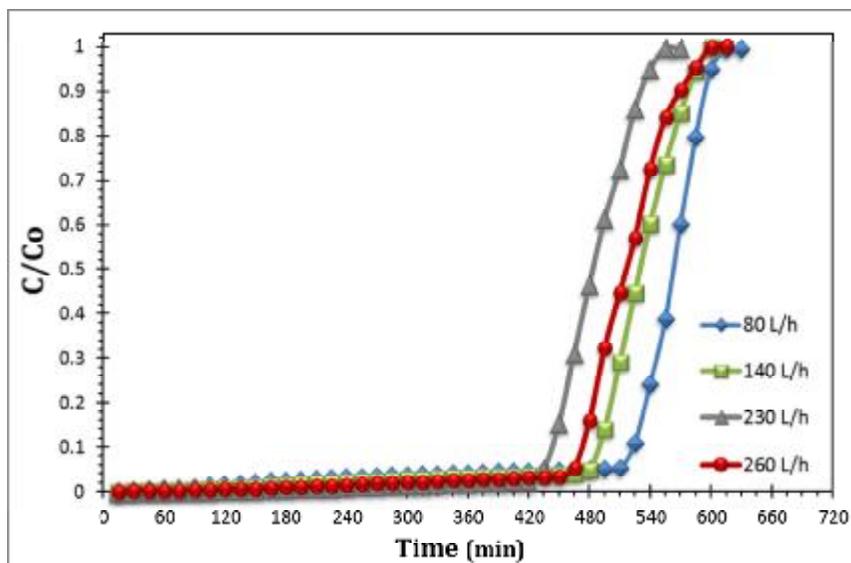


Figure (4): Breakthrough Curves of 7Ni/AC Catalyst with Different Flue Gas Flow Rates at Bed Height of 8cm.

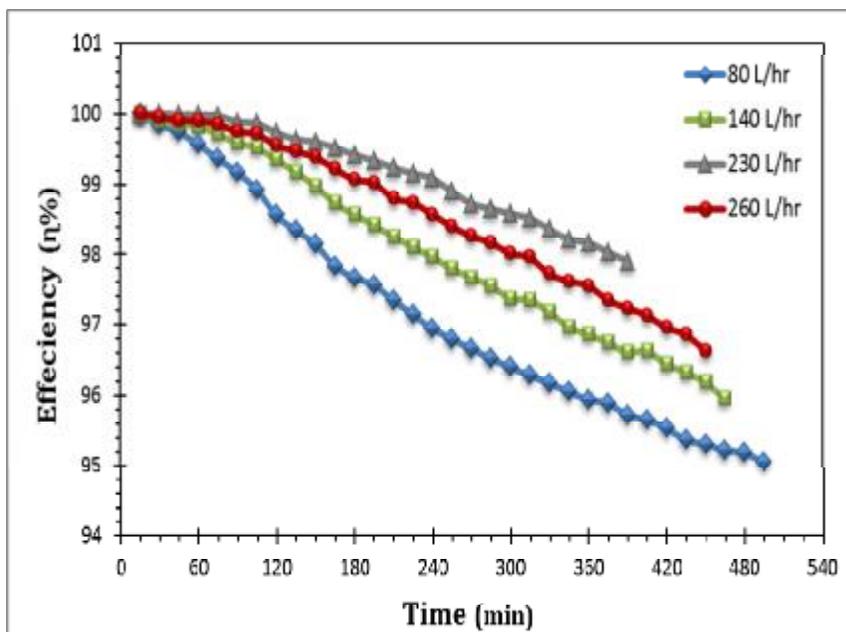


Figure (5): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Flue Gas Flow Rates at Bed Height of 8cm.

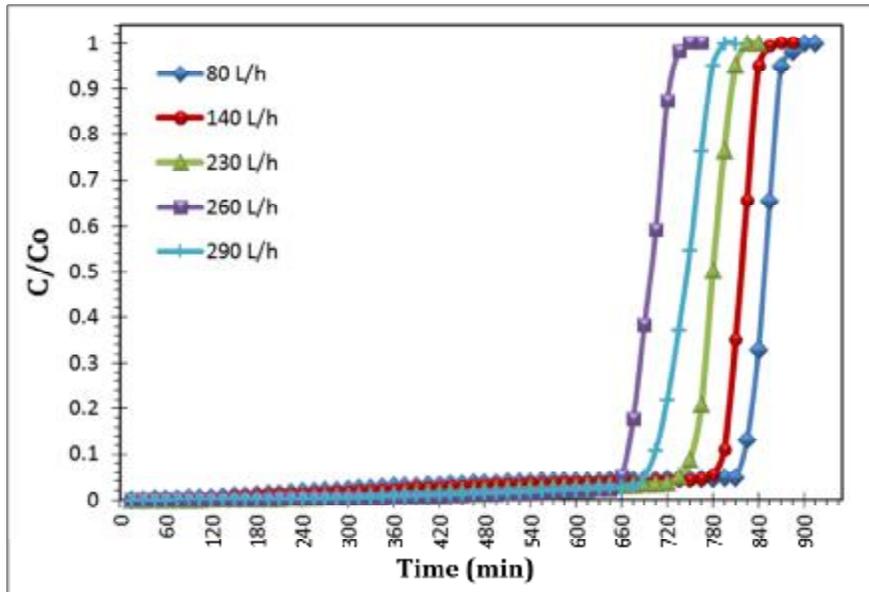


Figure (6): Breakthrough Curve of 7Ni/AC Catalyst with Different Flue Gas Flow Rates at Bed Height of 12 cm.

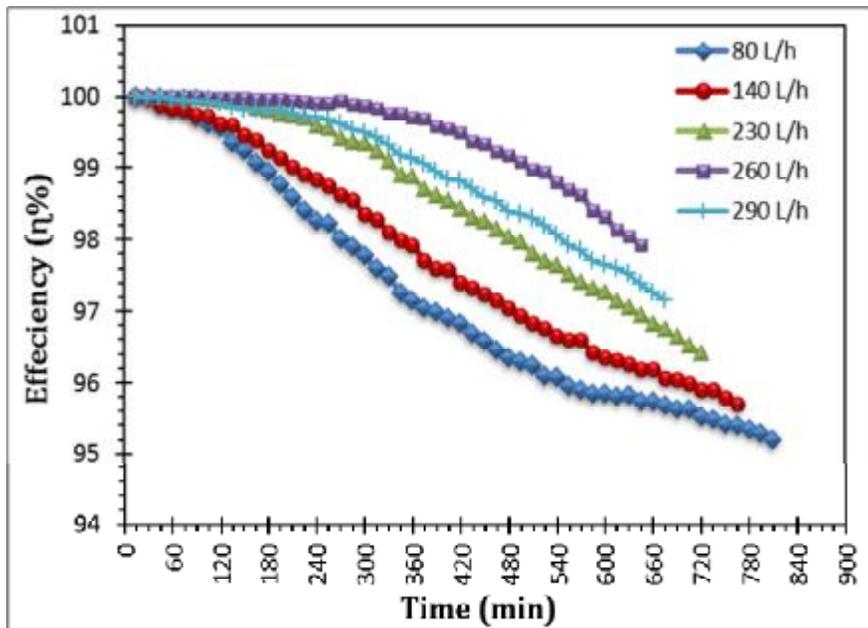


Figure (7): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Flue Gas Flow Rates at Bed height of 12cm.

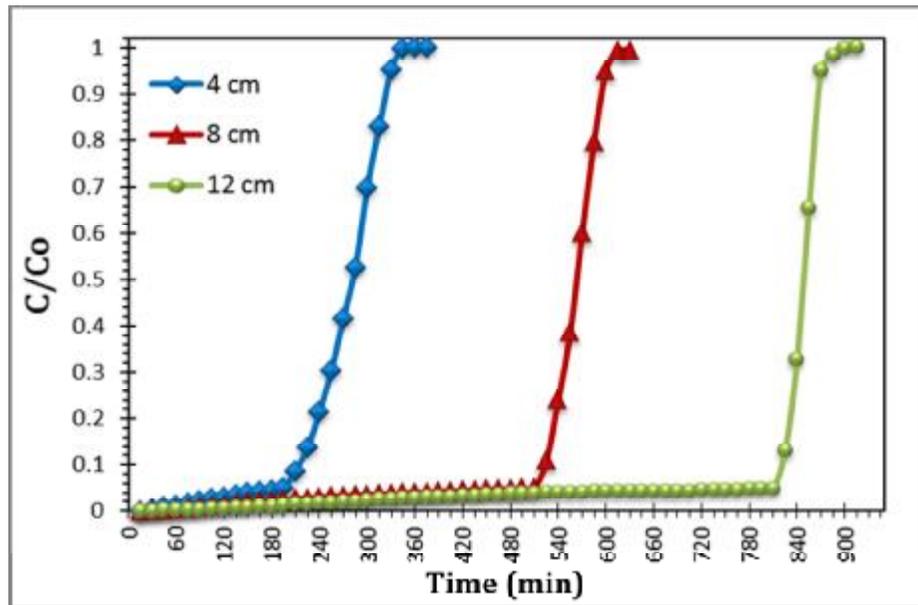


Figure (8): Breakthrough Curves of 7Ni/AC Catalyst for Different Bed Heights at Gas FlowRate 80 l/h.

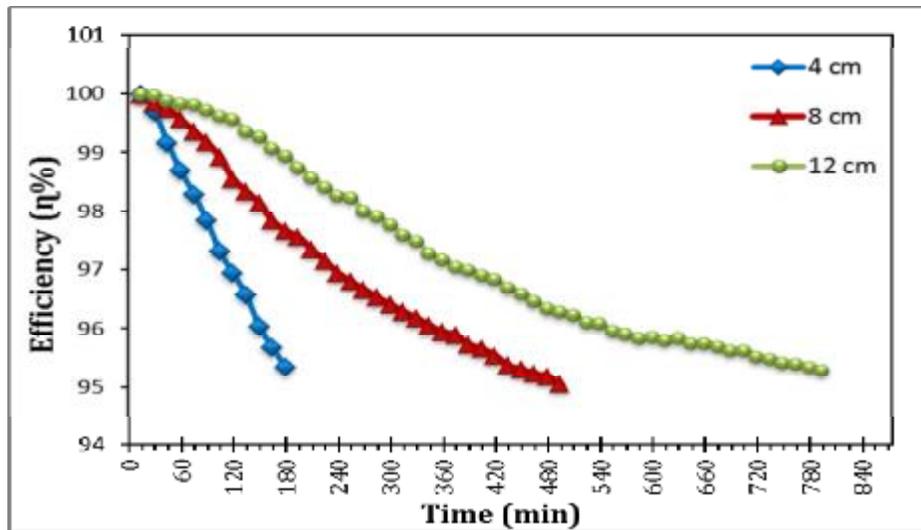


Figure (9): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Bed Heights at Gas Flow Rate 80 l/h.

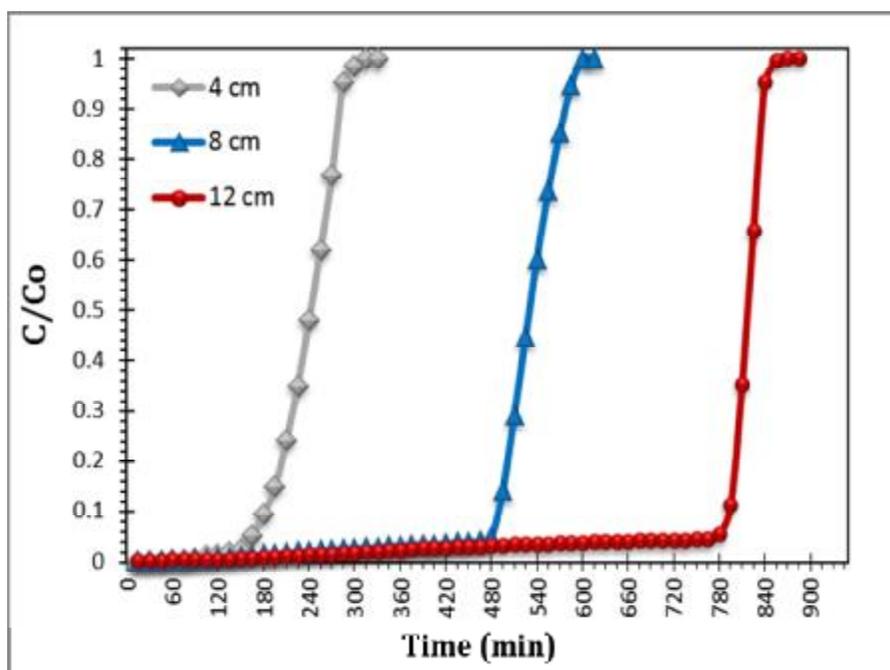


Figure (10): Breakthrough Curves of 7Ni/AC Catalyst for Different Bed Heights at Gas Flow Rate 140 l/h.

Effect of Bed Height

Figures (8) to (15) illustrate the change in SO₂ sorption breakthrough and SO₂ removal efficiency with time using 7Ni/AC catalyst at different gas flow rates. The trend of the results show that with increasing bed heights the effluent concentration of SO₂ decreases, the breakthrough time and SO₂ removal efficiency increase for different gas flow rates. This behavior was also observed by Liu and Kato [19] and Elias [20].

At gas flow rate of 80 l/h and retention time of 180 minutes (3h), increasing the bed height from 4 to 12cm decreased the effluent concentration of SO₂ from 116ppm to 26ppm and increased the breakthrough time from 3 h to 13 h. Since both gas rate and inlet SO₂ concentration are constant, on increasing the bed height, the contact time between the polluted gas and the sorbent increases. Moreover, the sorbent surface area increases and more active sites will be available which enhance SO₂ removal efficiency.

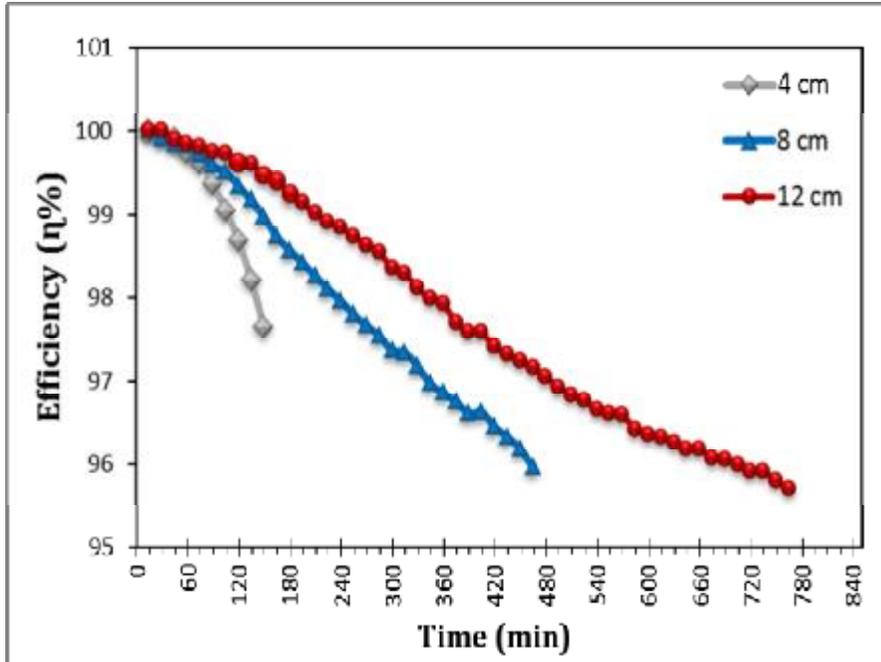


Figure (11): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Bed Heights at Gas Flow Rate 140 l/h.

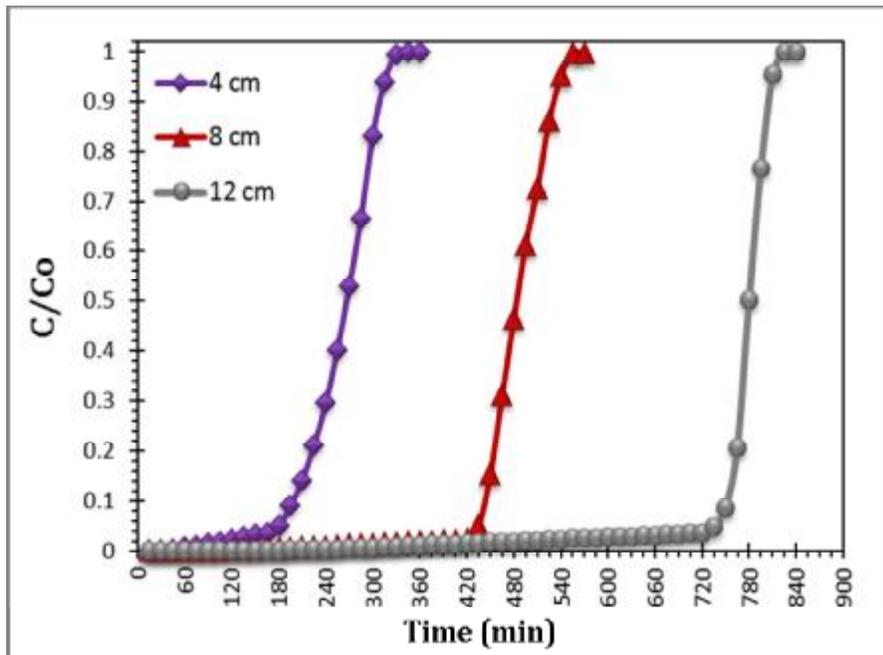


Figure (12): Breakthrough Curves of 7Ni/AC Catalyst for Different Bed Heights at Gas Flow Rate 230 l/h.

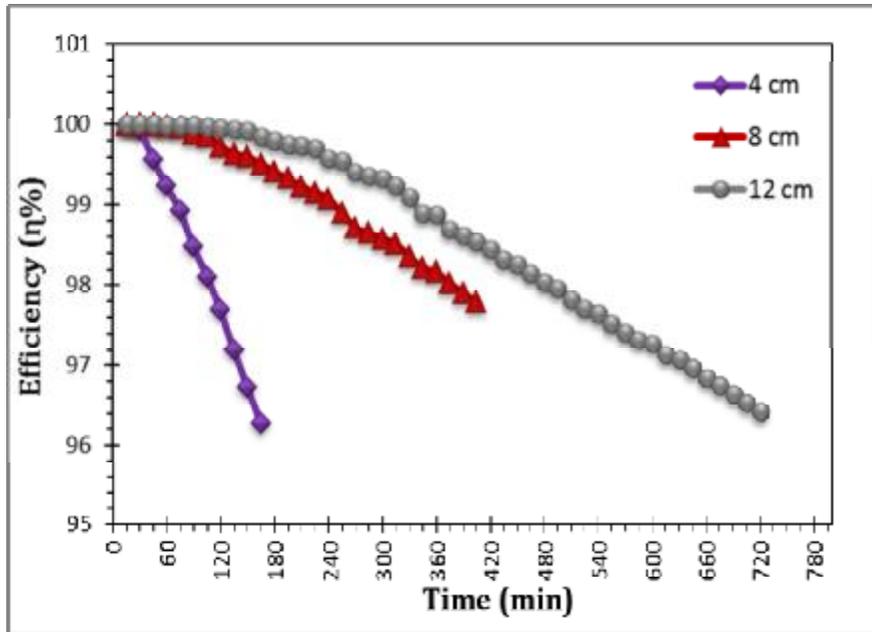


Figure (13): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Bed Heights at Gas Flow Rate 230^l /h.

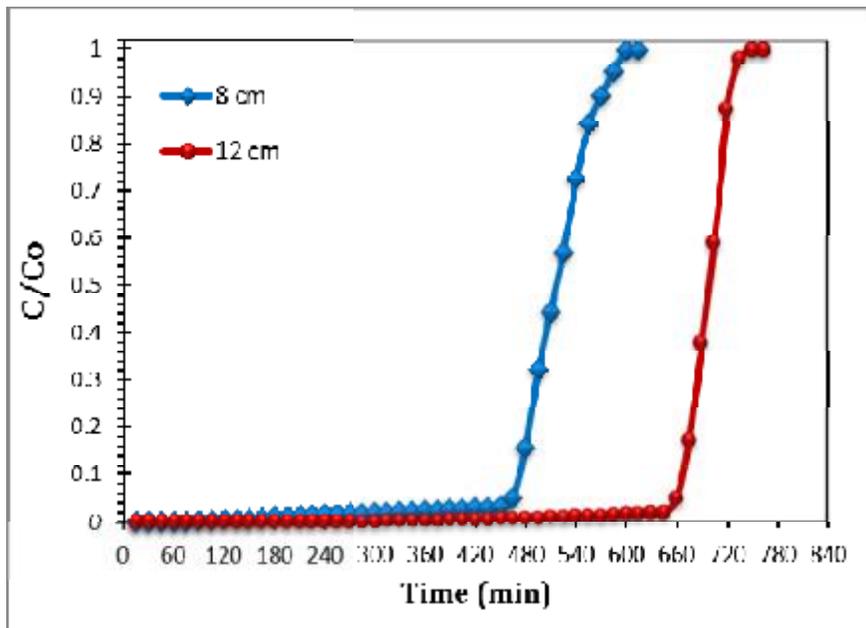


Figure (14): Breakthrough Curves of 7Ni/AC Catalyst for Different Bed Heights at Gas Flow Rate 260^l /h.

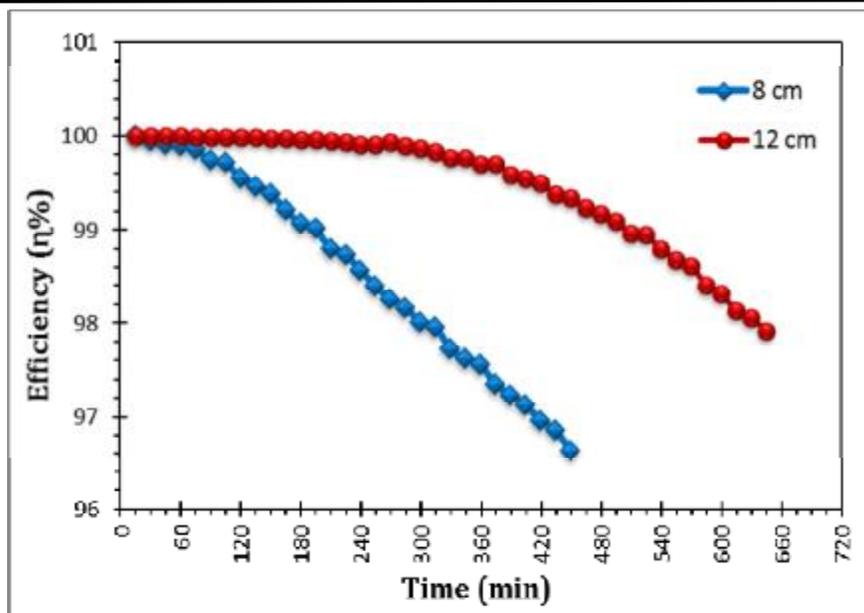


Figure (15): Change in SO₂ Removal Efficiency of 7Ni/AC Catalyst with Time for Different Bed Heights at Gas Flow Rate 260 l/h.

Length of mass transfer zone L_{MTZ}

The characteristic parameters derived from breakthrough curves for two different bed heights (8 and 12cm) operating at different superficial gas velocities are listed in Table (3). It may be observed from the table that on increasing superficial gas velocity two regions are developed. In the first region: when the superficial gas velocity increased the breakthrough time and the exhaustion time decreased but the L_{MTZ} was prolonged (diffusion control). While in the second region, the breakthrough time, exhaustion time and L_{MTZ} increased as the superficial gas velocity increased (reaction control).

Table (3): Effects of Superficial Gas Velocity on the Characteristic Parameters.

• At Bed Height 8 cm

Superficial Gas velocity (cm/min)	Breakthrough Time $\tau_{0.05}$ (min)	Exhaustion Time $\tau_{0.95}$ (min)	Length of MTZ L_{MTZ} (cm)
263	818	870	0.74
462	780	840	0.89
758	739	810	1.1
857	660	730	1.21
955	695	780	1.38

- At Bed Height 12 cm

Superficial Gas velocity (cm/min)	Breakthrough Time $\tau_{0.05}$ (min)	Exhaustion Time $\tau_{0.95}$ (min)	Length of MTZ L_{MTZ} (cm)
263	510	600	1.3
462	488	590	1.51
758	435	540	1.72
857	465	585	1.83

The superficial gas velocity of flue gas is a critical factor to determine the L_{MTZ} . As shown in Figure (16), the L_{MTZ} increases with increasing the superficial gas velocity. This behavior is attributed to the fact that increasing the superficial gas velocity improves the mass transfer in the gas phase across the boundary layer, but does not affect intra-particle mass transfer (affected by particle size or shape), thus increasing the MTZ thickness [21, 22]. Figure (17) shows the effect of bed heights on L_{MTZ} for different superficial gas velocities. The results indicate that as the bed height increased, the L_{MTZ} decreased for the all tested superficial gas velocities. This is due to the fact that the increase in bed height provides more surface area and active sites to adsorb species (i.e. length of active zone was longer than the length of mass transfer zone) [21].

Table (4): Effects of Nitric Acid Concentrations on Characteristic Parameters.

Acid Concentrations wt%	Breakthrough Time $\tau_{0.05}$ (min)	Exhaustion Time $\tau_{0.95}$ (min)	Length of MTZ L_{MTZ} (cm)
0 (7Ni/AC)	165	285	2.13
10 (7Ni/10NAC)	210	330	1.78
45 (7Ni/45NAC)	285	390	1.24

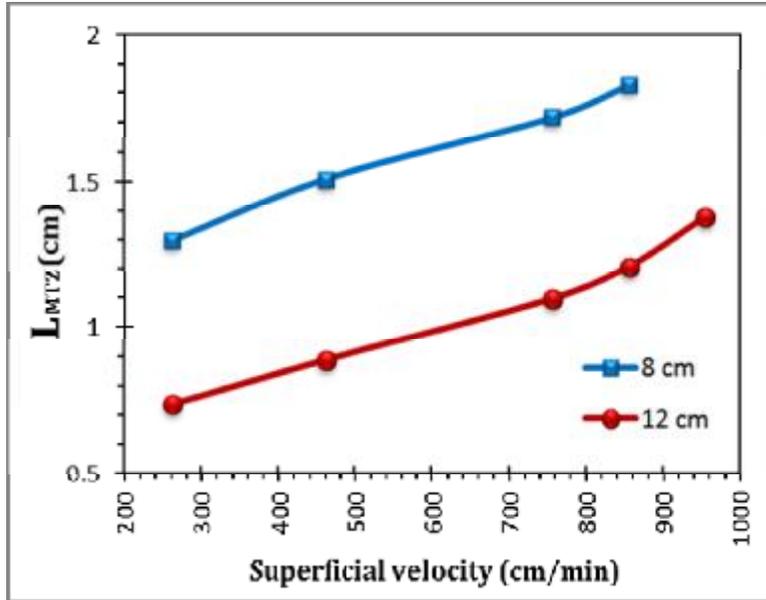


Figure (16): Effect Superficial Gas Velocities on L_{MTZ} for 7Ni/AC Catalyst and Different Bed Heights.

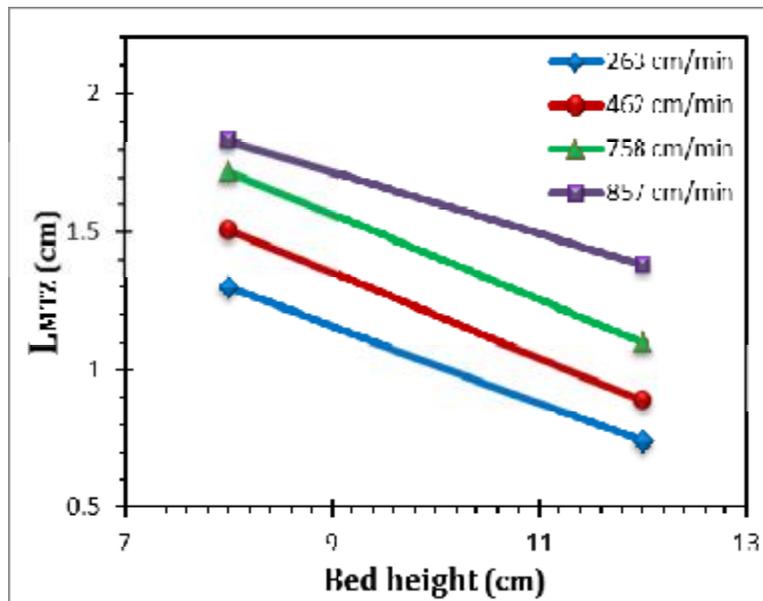


Figure (17): Effect of Bed Heights on L_{MTZ} for 7Ni/AC Catalyst with Different Superficial Gas Velocities.

The effect of treating AC with 10 and 45% HNO₃ on L_{MTZ} is presented in Table(4), indicate that L_{MTZ} decreased by about 42% and, the breakthrough and exhaustion time increased by about 73% and 37% respectively, when the original AC was treated with 45 wt% HNO₃. This change may be attributed to the modifications in the physical and chemical properties of AC when treated with nitric acid. The treatment of AC by HNO₃ enhances the properties of AC by producing more functional groups as active sites, (interior) decreasing the diffusional resistance and hence shorting the length of MTZ. These findings are in agreement with Lisovski et al [23] and Xianglan et al.[24].

Based on the experimental results, an empirical expression for length of mass transfer zone in terms of superficial gas velocity and bed height was suggested as in equation (3). STATISTICA software was applied. A non-linear numerical method, Quasi-Newton method, was used as regression method. The differences between experimental data and corresponding calculated results indicate the reliability of correlation. Determination coefficient, R, was used to quantify the accuracy of regression.

$$L_{MTZ} = \frac{1.58 V_g^{0.35}}{H^{1.06}} \dots (3)$$

The corresponding correlation coefficient, variance, standard deviation and error were 0.9813, 0.9629, 0.3601 and 0.1200 respectively.

CONCLUSIONS

The optimum values of flue gas flow rates can be observed from the experimental results at 140, 230 and 260 ℓ /h for bed heights of 4, 8 and 12 cm, respectively. L_{MTZ} decreased with increasing the concentration of HNO₃ used. Better performance can be obtained when operating with longer columns and lower superficial gas velocity.

Notation

Symbol	Description	Unit
C	Exit SO ₂ Concentration	ppm
C _o	Initial SO ₂ Concentration	ppm
H	Bed height	cm
L _{MTZ}	Length of Mass Transfer Zone	cm
Q	Gas Flow Rate	ℓ/h
V _g	Gas Superficial Velocity	cm/min
τ _{0.05}	Breakthrough time	min
τ _{0.95}	Exhaustion time	min

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