

## Desulphuration of SO<sub>2</sub> by Adsorption in Fluidized Bed with Zeolite

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Desulphuration of SO<sub>2</sub> experiments were carried out in a fluidized bed using a high ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> zeolite as adsorbent. The SO<sub>2</sub> adsorption efficiency on this zeolite was analyzed employing the hydrogen peroxide method. The desulphuration experiments were conducted using 16 grams of adsorbent and 2400 ppm of SO<sub>2</sub>. This ratio of adsorbent mass to SO<sub>2</sub> concentration was determined by a Two-level Factorial Planning as the best condition for treating the gas in the fluidized bed. The experimental results permitted the determination of adsorption capacities and the equilibrium data of SO<sub>2</sub> adsorption on silicalita zeolite. Comparatively the adsorption under fluidization is a faster process than in fixed bed. The dynamic adsorption isotherm obtained was well fitted by the Freundlich equation.

### 1. Introduction

The air quality in several countries has been affected by ambient atmospheric concentrations of criteria pollutants, notably total suspended particles (TSP), sulfur dioxide (SO<sub>2</sub>) (Lee, *et al.*, 2008; Vet and Ro, 2008; Benko, *et al.*, 2007), and nitrogen dioxide (NO<sub>2</sub>). Among the several atmospheric pollutants the sulphur dioxide has been receiving a special attention of the world government public organs due to the severity of its effects on the people, on the animals or on the vegetation (Gurjar, *et al.*, 2008).

The use of the adsorption as an alternative process for purification of gaseous pollutant emissions. Nowadays, the removal of the sulphur dioxide by the adsorption in a solid adsorbent has a good potential application (Pulido and Fernández, 2007; Gupta, *et al.*, 2004).

In comparison to fixed bed, the employment of fluidized bed for adsorption process presents as advantage a better gas-solid contact, which propitiates a better coefficient of mass transfer.

The zeolite silicalita type is a molecular sieve with hydrophobic and organophilic characteristics, has great stability to most of the mineral acids and also the necessary oxidized conditions for its regeneration. Its crystalline structure presents characteristics that make possible its use as adsorbent in processes of SO<sub>2</sub> removal from combustible gases.

Several researchers (Allen, *et al.*, 2009; Ivanova and Koumanova, 2009; Gupta, *et al.*, 2004; Tribranka and Assenov, 2000) carried out studies on adsorbents, more

specifically using zeolites, involving the adsorption of pollutants gases (e.g. CO<sub>2</sub>, SO<sub>2</sub>, organic solvent vapors, along with other gases).

In this work, zeolite with high ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was used as adsorbent in the process of SO<sub>2</sub> removal from a gaseous current, using the air as carrier gas. It was employed the silicalita, a zeolite belonging to the pentasil group, with the type MFI structure. The employment of this molecular sieve is due basically to two main aspects: first, its hydrophobic characteristic, once the presence of water acts as a strong competitor of the active porous for the most of the aluminosilicates, generally hydrophilics, and the second, the possibility of working at low temperatures.

The adsorption process of SO<sub>2</sub> was accomplished in an experimental system of fluidized bed, using the acidimetric or the hydrogen peroxide method for the analysis of the final concentration of the SO<sub>2</sub>.

## 2. Material and Method

The experimental development of this work had as base a complete factorial planning of two levels, in which it was obtained the operational and the process conditions more adapted to the removal of the SO<sub>2</sub>. These adequate conditions were: the adsorbent mass equal to 16 g, the concentration of SO<sub>2</sub> in the feeding stream of 2400 ppm for an operation flow rate of 2000 mL/min and 0.31 mm diameter for the zeolite particles.

According to Medeiros et al. (2009), the thermal treatment in same type of silicalita zeolite does not have any effect on its SO<sub>2</sub> removal capacity SO<sub>2</sub>. Because of this, the silicalita zeolite was used in the experiments without thermal treatment. The physical properties of silicalita were obtained by the BET analysis, He picnometry and Hg porosimetry analysis. The properties obtained from these analyses and particle size can be visualized in Table 1.

*Table 1: Zeolite superficial area (BET), porosity ( $\epsilon'$ ), average particle diameter  $D_p$ , particle porous diameter ( $d_{pi}$ ), average particle diameter  $d$  and porous volume ( $V_p$ ).*

Zeolite	$d_{pi}$ ( $\mu\text{m}$ )	$D_p$ (mm)	$\epsilon'$	$V_p$ (mL/g)	BET (m <sup>2</sup> /g)
Silicalita	0.097	0.31	0.54	0.814	306.79

The experimental system used to carry out desulphuration of air containing SO<sub>2</sub> was a bubbling fluidized bed consisting of 3 cm ID column having 50 cm of height. The column of adsorption was fed by an air stream containing SO<sub>2</sub>, using a flow rate 2000 mL/min. The temperature of this gaseous stream was maintained at 25 °C. The experimental procedure was developed in the conditions previously mentioned: The time of operation was 70 minutes.

The analysis of the sulphur dioxide (SO<sub>2</sub>) was developed by using the Orsat apparatus with 16 impingers for the gas collection, which were maintained in thermostatic bathing. The acidimetric method (Leithe, 1971) was used to analyze the SO<sub>2</sub> entrapped into these impingers containing 3% w/w hydrogen peroxide.

As the air volume is sampled in the Orsat apparatus, the solution of hydrogen peroxide inside the impinger absorbed the sulphur dioxide, transforming it into H<sub>2</sub>SO<sub>4</sub>. The

number of moles of the solute  $\text{SO}_4^{2-}$  present in the hydrogen peroxide solution is the same as that of the sulphur dioxide absorbed from the air volume sampled.

The effect of the acidity of the plain 3% hydrogen peroxide solution was previously determined with a titration using standard sodium hydroxide 0.1 N. The volume used in this titration ( $V_B$ ) was reduced from the total volume of sodium hydroxide ( $V_T$ ) used in the titration of the solution containing absorbed sulphur dioxide.

The number of moles of sulphur dioxide ( $n_{\text{SO}_2}$ ) present in the sampled air was obtained by using equation (1). As the titrations were accomplished with aliquots of 50 mL from the solution of 1000 mL, a factor equal 20 was introduced in this equation to correct the number of moles of sulphur dioxide.

$$n_{\text{SO}_2} = 20 N (V - V_B) / 2 \quad (1)$$

The total number of moles of air mixture ( $n_T$ ) was determined by the Eq. (2) and the molar fraction of sulphur dioxide was obtained according to equation (3).

$$n_T = \frac{V_T}{V} \quad (2)$$

$$F_{\text{SO}_2} = \frac{20 V N (V - V_B)}{2 V_T} \quad (3)$$

Adsorption experiments were carried out in the fluidized bed to obtain the breakthrough curve and the dynamic adsorption isotherm. The amount of useful and total removal were calculated, which correspond to the capacity of metal removal until the breakthrough point ( $q_U$ ) and saturation point ( $q_T$ ), respectively. Eqs. (4) and (5) were obtained through mass balance in the column using its saturation data based on its breakthrough curves, where the area below the curve  $(1 - C/C_0)$  until the breakthrough point is proportional to  $q_U$ , and until the bed exhaustion is proportional to  $q_T$ :

$$q_U = \frac{C_0 Q_0 M_{\text{SO}_2}}{m_S V_m} \int_0^{t_b} \left( 1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (\text{g/g}) \quad (4)$$

$$q_T = \frac{C_0 Q_0 M_{\text{SO}_2}}{m_S V_m} \int_0^{t_{\text{tot}}} \left( 1 - \frac{C|_{z=L}}{C_0} \right) dt \quad (\text{g/g}) \quad (5)$$

The amount adsorbed at each time  $t$  was obtained by:

$$q_{\text{SO}_2\text{ads}} = \frac{t C_0 Q_0 M_{\text{SO}_2}}{m_S V_m} \quad (\text{g/g}) \quad (6)$$

### 3. Results

Table 2 shows values experimental results of  $\text{SO}_2$  adsorption on silicalita particles under fluidization condition by 2000 mL/min of air at 25 °C, containing 2400 ppm of  $\text{SO}_2$ . The breakthrough curve obtained, presented in Figure 1, exhibits in its profile a narrow saturation resistance low, indicating good removal efficiency in the process. The values of  $q_U$  and  $q_T$  on silicalita were 2.76 and 7.75 g/g, respectively.

As observed in the removal kinetics curve, presented in Figure 1, the adsorption process occurs initially in a very fast manner up to 30 minutes. After 70 minutes the absorbent present in the fluidized bed is completely saturated. However, it is interesting to

emphasis that the adsorption upon the fluidizing condition, used in this study, occurred more rapidly. This is because the fluidization of particles in the bed improves the efficiency of the mass transfer during the adsorption process.

Table 2: Dynamic adsorption data of  $SO_2$  in silicalita particles.

t (min)	$F_{SO_2}$ ( $\times 10^{-6}$ )	P (mmHg)	$C_{SO_2}$ ( $mg/m^3$ )	$C/C_0$	% $SO_2$ Adsorbed	Cumulative $SO_2$ adsorbed (mg)	$p_{SO_2}$ (mmHg)	$q_{SO_2ads}$ (g/g)
10	105.54	820	276.28	0.044	95.60	57.06	0.086	3.57
15	293.69	821	768.82	0.122	87.76	84.63	0.24	5.29
20	724.74	822	1897.22	0.302	69.80	106.56	0.60	6.66
25	1482.89	822	3881.91	0.618	38.21	118.32	1.23	7.40
30	1840.13	820	4817.09	0.767	23.33	125.21	1.51	7.82
35	2078.55	821	5441.23	0.866	13.39	129.16	1.71	8.07
40	2099.88	821	5497.07	0.875	12.50	132.86	1.72	8.30
45	2117.54	822	5543.30	0.882	11.77	136.41	1.74	8.52
50	2205.68	820	5774.03	0.919	8.10	138.85	1.81	8.68
55	2289.20	821	5992.67	0.954	4.62	140.27	1.88	8.77
60	2310.96	822	6049.63	0.963	3.71	141.39	1.90	8.84
65	2389.98	822	6256.49	0.996	0.42	141.52	1.96	8.85

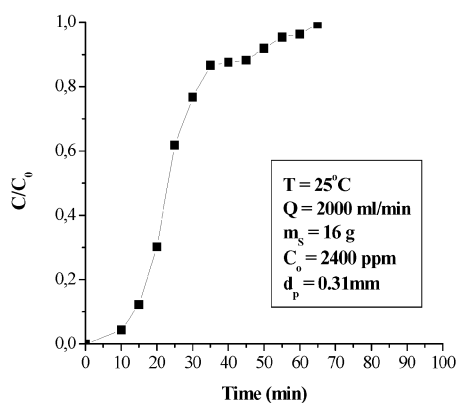


Figure 1: Breakthrough curves of  $SO_2$  in zeolite.

The data of the obtained dynamic isotherm were fitted to the Langmuir and Freundlich models through the non-linear regressions of Equations (6) and (7), respectively. An illustration of this fitting is presented in Figure 2. The parameter  $q_m$  of Langmuir indicated maximum capacity of 9.2 g/g ( $R^2 = 0.980$ ). The values of Freundlich model parameters  $K$  and  $n$  were of 7.28 and 0.27, respectively. The data fitted very to this model as a correlation coefficient  $R^2$  of 0.990 was obtained. These results are in agreement with those presented by Tantet (1993), who also found a high correlation coefficient ( $R^2 = 0.995$ ) in fitting the Freundlich model for isotherm data for  $SO_2$  adsorption on fixed bed. The good fitting of data obtained in this work to the Freundlich model is probably due to the data being quite closer to the lineal region of the Henry's law.

$$q_{SO_2_{ads}} = \frac{q_m \cdot b \cdot p}{1 + b \cdot p} \quad (6)$$

$$q_{SO_2_{ads}} = K p^n \quad (7)$$

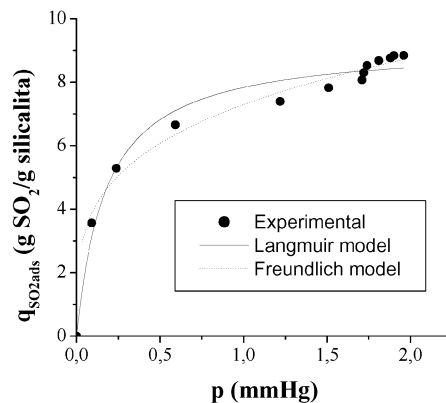


Figure 2: Adsorption isotherm of  $SO_2$  fitted by Langmuir and Freundlich Equations.

#### 4. Conclusions

From the results of this work it can be concluded that: the fluidized bed used in this work for the desulphuration of  $SO_2$  presented a satisfactory performance to the adsorption process studied.

The adsorption process conducted under fluidization occurred more rapidly, presenting low mass transfer resistance, due to the fluid dynamic of this system.

The largest removal of  $SO_2$  occurred in the first 20 minutes of process and the complete saturation of the fluidized bed occurs after 70 minutes and the time of breakthrough occurred at 10 minutes.

The isotherm of adsorption was very well fitted to Langmuir and Freundlich models. A behavior that can be justified by the majority of the data be in the lineal region corresponding to Henry's law.

The profile of the breakthrough curve obtained corresponds to a narrow zone of mass transfer in relation to the bed length, indicating that the largest capacity of the solid can be used, contemplating in a good efficiency of the process.

The adsorption capacity of  $SO_2$  for the silicalita obtained was of 9.2 g/g, being comparable with the result obtained by Chriswell and Gjerde (1982) using the same physical adsorbent in a fixed bed for the  $SO_2$  removal.

#### 5. Nomenclature

Q - flow rate of the gaseous mixture in the analyzer,  $cm^3/min$ .

t - time of analysis, min.

$\underline{V}$  - molar volume molar of the mixture at analysis temperature and pressure,  $cm^3/mol$ .

$V_T$  - total volume of gas measured by the gasholder,  $cm^3$ .

N - soda normality, N.

V - volume of soda used in the titration of the solution, L.

$V_B$  - volume of used in the white titration, L.

$q_U$  - useful capacity, g of  $SO_2/g$  of adsorbent.

$q_T$  - dynamic capacity, g de SO<sub>2</sub>/g of adsorbent.  
 $t_b$  - breakthrough time, min.  
 $t_{tot}$  - stoichiometric time, min.  
 $C_o$  - entrance concentration, L SO<sub>2</sub>/L of gas.  
 $Q_o$  - flow rate through the column, L/min.  
 $M_{SO_2}$  - molar weight of SO<sub>2</sub>, g/mol.  
 $m_s$  - mass of dry adsorbent in the column, g.  
 $V_m$  - molar volume of an ideal gas at 25°C and 1 atm, L of SO<sub>2</sub>/mol.  
 $p_{SO_2}$  - partial pressure of SO<sub>2</sub> in the gaseous current of outflow of the bed, mm Hg.  
 $F_{SO_2}$  - molar fraction of SO<sub>2</sub> in the gaseous flow obtained by the acidimetric method, (-).  
 $P$  - total pressure of the system, mm Hg (experimental measure).  
 $p$  - total pressure of the system, mmHg.  
 $q_{SO_2ads}$  - amount of SO<sub>2</sub> adsorbed per unit of adsorbent mass, g/g.  
 $q_m$  - amount maximum of SO<sub>2</sub> adsorbed in monolayer, g/g.  
 $b$  - Langmuir constant.  
 $K, n$  - Freundlich constants.

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