DESULPHURATION OF SO_2 BY ADSORPTION IN FLUIDIZED BED WITH ZEOLITE

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Abstract: Desulphuration of SO_2 experiments were carried out in a fluidized bed using a high ratio SiO_2/Al_2O_3 zeolite as adsorbent. The SO_2 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_2. This ratio of adsorbent mass to SO_2 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_2 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.

Keywords: Atmospheric pollutants treatment; Adsorption of SO_2; Adsorption in fluidized bed.

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_2), and nitrogen dioxide (NO_2) (Gurjar, *et al*., 2008). 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.

The impact of sulfur dioxide emissions in the Asian continent (from industries, vehicular emissions and dust storms) (Lee, *et al.,* 2008; Cai and Xie, 2007) as well in North America (Vet and Ro, 2007) and in Europe (De Meyer, *et al*., 2008; Benko, *et al.*, 2007) continents on the air quality has been object of several studies.

The use of the adsorption with practical application of its properties for separation in great scale and purification of materials of industrial processes is relatively recent. This process has shown advantages as an alternative process so much from the point of view of costs as well as the selectivity for several processes aiming treatment and purification of gaseous pollutant emissions. Nowadays, the removal of the sulphur dioxide by the adsorption in a solid adsorbent has a good application potential (Pulido and Fernández, 2007; Gupta, *et al*., 2004). The adsorption process can be accomplished using a bed or a column, either fixed or mobile, as the fluidized, of porous granular particles or permeable particles. These particles selectively remove a desirable component (valuable or even without value component) from a gaseous or liquid stream feeding the bed or column (Mcketta, 1993). 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 research of the adsorbent, in general, is the first step in the development of the adsorption process. The adsorbent selection for a process is still a complex problem, and its choice is associated to its selectivity, its adsorption capacity and its lifetime. These properties depend, firstly, on the adsorption kinetics and on the equilibrium adsorption. The selectivity kinetic is measured by the ratio of the intra-crystalline diffusivities or of the micro porous for components to be considered, in agreement with their physical properties (Knaebel, 1995).

Among the several adsorbents found in the market, the zeolite silicalita type has its importance for being of a molecular sieve with hydrophobic and organophilic characteristics, to present 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_2 removal from combustible gases.

Several researchers (Gupta, *et al*., 2004; Tribranka and Assenov, 2000; Webb and Orr, 1997; Reichhold and Rofbauer, 1995; Diaf and Beckman, 1999; Shutz-Siebbel, *et al*., 1992) carried out studies on adsorbents, more specifically using zeolites, involving the adsorption of pollutants gases (e.g. CO_2, SO_2, organic solvent vapors, along with other gases).

In this work, zeolite with high ratio SiO_2/Al_2O_3 was used as adsorbent in the process of SO_2 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_2 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_2.

2. MATERIALS AND METHODS

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_2. These adequate conditions were: the adsorbent mass equal to 16g, the concentration of SO_2 in the feeding stream of 2400ppm for an operation flow rate of 200mL/min and 0.31mm diameter for the zeolite particles.

According to with Medeiros (2001), the thermal treatment in same type of *silicalita* zeolite does not have any effect on its SO_2 removal capacity SO_2. Because this, the *silicalita* zeolite were used in the experiments without thermal treatment. The physical properties of *silicalita* were obtained by the BET analysis, Helium picnometry and mercury porosimetry analysis. The properties obtained from these analyses and particle size can be visualized in Table 1.

Table 1. Zeolite superficial area (BET), porosity (ε'), average particle diameter Dp, particle porous diameter (dp_i), average particle diameter d and porous volume (V_p).

Zeolite	dp_i (µm)	Dp (mm)	ε'	V_p (mL/g)	BET (m^2/g)
Silicalita	0.097	0.31	0.54	0.814	306.79

The experimental system used to carry out desulphuration of air containing SO_2 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_2, using a flow rate 2000 mL/min. The temperature of this gaseous stream was maintained at 25ºC. The experimental procedure was developed in the conditions previously mentioned: The time of operation was 70 minutes.

The analysis of the sulphur dioxide (SO_2) was developed by using the Orsat apparatus with 16 impingers for the gas collection, which were maintained in thermostatic bathing. The acidimetric method (Tomaz, 1990; Leithe, 1971) was used to analyze the SO_2 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_2SO_4. The number of moles of the solute 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_{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 1000ml, a factor equal 20 was introduced in this equation to correct the number of moles of sulphur dioxide.

$$n_{SO_2} = 20\,N\,(V - V_B)/2 \quad (1)$$

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).

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

$$F_{SO_2} = \frac{20\,\underline{V}\,N\,(V - V_B)}{2\,V_T} \quad (3)$$

The concentration of sulphur dioxide in the air stream in units of ppm and of mg per cubic meter was obtained from the corresponding mole fraction multiplied by the factors: (10^6) and ($10^6/0.382$), respectively.

Adsorption experiments were carried out in the fluidized bed to obtain the breakthrough curve and the dynamic adsorption isotherm. From breakthrough curve both the rupture and estoichiometric times were obtained for the fluidized bed.

The equilibrium adsorption capacity (q*) and the dynamic adsorption capacity (q') for the adsorption process were calculated using equations (4) and (5), which are based on simple mass balance disregarded accumulation into gaseous phase.

$$q^* = \frac{t^* \, C_o \, Q_o M_{SO_2}}{m_S \, V_m} \quad \text{(g/g)} \qquad (4)$$

$$q' = \frac{t' \, C_o \, Q_o \, M_{SO_2}}{m_S \, V_m} \quad \text{(g/g)} \quad (5)$$

3. RESULTS AND DISCUSSION

The experimental results of SO_2 adsorption on silicalita particles under fluidization condition by 2000 ml/min of air at 25°C, containing 2400 ppm of SO_2 are shown in Table 2. The breakthrough curve obtained, presented in Figure 1, exhibits in its profile a narrow zone of mass transfer in relation to the bed length indicating good removal efficiency in the process. It can be observed in this curve that the rupture time (t') and the stoichiometric time (t*) for the adsorption process occurs respectively in 10 and 20 minutes. Determination of the t' and t* values, allowed to calculate the equilibrium and dynamic adsorption capacities by using the Eqs. (4) and (5). The values of these capacities are, respectively: 17.28 and 8.64 mg of SO_2 per gram of silicalita.
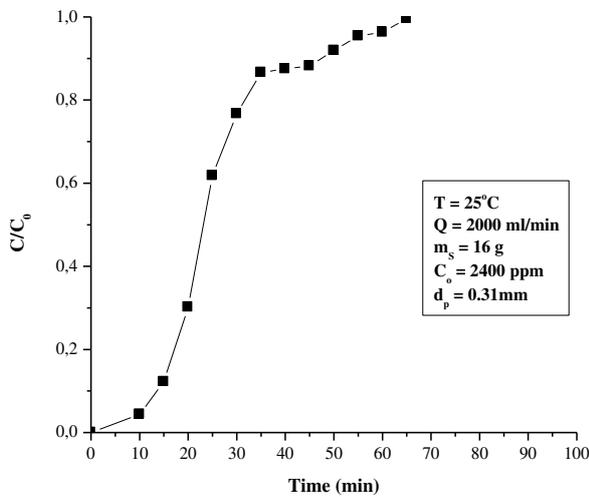
Fig. 1. Experimental breakthrough curve for SO_2.

Tantet (1993) and Chriswell and Gjerde (1982) also studied the adsorption process of SO_2 with the employment of the silicalita high ratio SiO_2/Al_2O_3 in a fixed bed. The values of equilibrium adsorption capacity obtained by these authors, respectively, were equal to 17.7 mg/g and 20 mg/g. These values are comparable to the value obtained in the present work. However, it is interesting to emphasis that the adsorption upon the fluidizing condition, used in this work, occurred more rapidly. This is because the fluidization of particles in the bed improves the efficiency of the mass transfer during the adsorption process.

As observed in the removal kinetics curve, presented in Figure 2, 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.
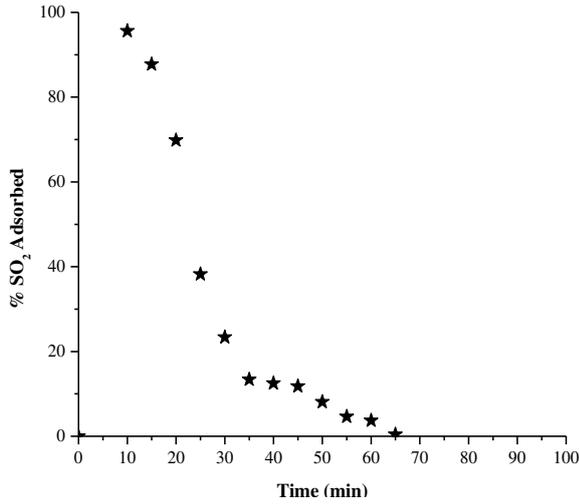
Fig. 2. Adsorption kinetics of SO$_2$ in function of the time.

The Experimental data concerning the SO$_2$ adsorption on silicalita presented in Table 2 allowed determining data for the dynamic isotherm, which are presented in Table 3. The partial pressure of SO$_2$ presented was calculated from the values mole fraction and total pressure measured. The amount in milligrams of SO$_2$ adsorbed on 16 grams of silicalita adsorbent of was computed cumulatively for each time. This quantity was obtained cumulatively from the difference between the previous and subsequent concentrations of SO$_2$, multiplied by the volume of gas (Medeiros, 2001)

Table 2. Adsorption results for the experimental conditions.

Time (min)	F_{SO2} (x10^{-6})	P (mm Hg)	C_{SO2} (mg/m^3)	C/C$_0$	% SO$_2$ Adsorbed
10	105.54	820	276.28	0.044	95.60
15	293.69	821	768.82	0.122	87.76
20	724.74	822	1897.22	0.302	69.80
25	1482.89	822	3881.91	0.618	38.21
30	1840.13	820	4817.09	0.767	23.33
35	2078.55	821	5441.23	0.866	13.39
40	2099.88	821	5497.07	0.875	12.50
45	2117.54	822	5543.30	0.882	11.77
50	2205.68	820	5774.03	0.919	8.10
55	2289.20	821	5992.67	0.954	4.62
60	2310.96	822	6049.63	0.963	3.71
65	2389.98	822	6256.49	0.996	0.42

Table 3. Computed values of the dynamic adsorption isotherm of SO$_2$ in silicalita particles.

Time (min)	F_{SO2}	P (mmHg)	C_{SO2} (ppm)	Cumulative SO$_2$ adsorbed (mg)	p_{SO2} (mmHg)	q_{SO2ads} (mg/g)
10	0.0001	820	105.54	57.06	0.086	3.57
15	0.0002	821	293.69	84.63	0.24	5.29
20	0.0007	822	724.74	106.56	0.60	6.66
25	0.0014	822	1482.89	118.32	1.23	7.40
30	0.0018	820	1840.13	125.21	1.51	7.82
35	0.0020	821	2078.55	129.16	1.71	8.07
40	0.0021	821	2099.88	132.86	1.72	8.30
45	0.0021	822	2117.54	136.41	1.74	8.52
50	0.0022	820	2205.68	138.85	1.81	8.68
55	0.0022	821	2289.2	140.27	1.88	8.77
60	0.0023	822	2310.96	141.39	1.90	8.84
65	0.0023	822	2389.98	141.52	1.96	8.85

The dynamic adsorption isotherm obtained is presented in Figure 3a, which shows its favorable character to remove the SO_2. The data of the obtained dynamic isotherm were fitted to the Freundlich model through the linearization of equation (6). An illustration of this fitting is presented in Figure 3b. The values of the model parameters K and n were 7.28 and 0.27 respectively. The data fitted very to this model as a correlation coefficient R^2 of 0.99045 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.

$$q = K\ p^{n} \qquad (6)$$

(a)   (b)
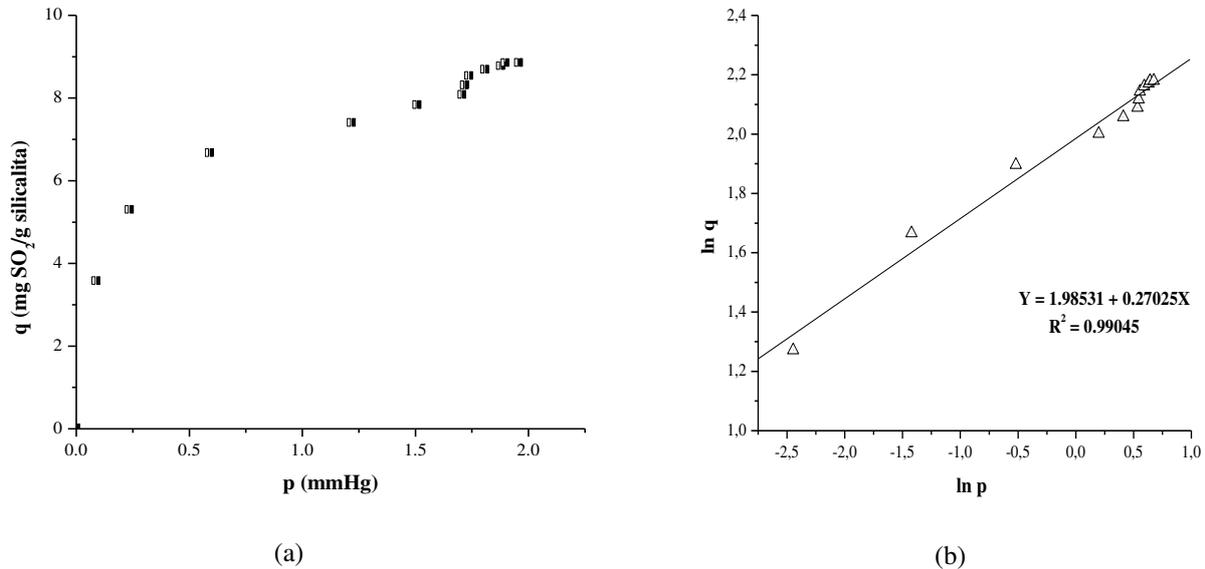
Fig. 3. (a) Adsorption isotherm, (b) Adsorption isotherm of SO_2 fitted by Freundlich Equation.

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.

Although the desulphuration of SO_2 in the fluidized bed provided results of removal close to those obtained using fixed bed, 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 rupture occurred at 10 minutes.

The isotherm of adsorption was very well fitted to Freundlich model. 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 17.28 mg/g, being comparable with the result obtained by Tantet (1993) and 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^* - equilibrium capacity, mg of SO_2/g of adsorbent.

q - dynamic capacity, mg de SO_2/g of adsorbent.

t´- rupture time, min.

t^* - stoichiometric time, min.

C_o - entrance concentration, L SO_2 / L of gas.

Q_o - flow rate through the column, L/min.

M_{SO2} - molar weight of SO_2, g/mol.

m_S - mass of dry adsorbent in the column, g.

V_m - molar volume of an ideal gas at 25ºC and 1 atm, L of SO_2/mol.

p_{SO2} - partial pressure of SO_2 in the gaseous current of outflow of the bed, mm Hg.

F_{SO2} - molar fraction of SO_2 in the gaseous current obtained by the acidimetric method, (-)

P - total pressure of the system, mm Hg (experimental measure)

p - total pressure of the system, mmHg.

q - amount of SO_2 adsorbed per unit of adsorbent mass.

6. ACKNOWLEDGEMENTS

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