SCIENTIFIC PAPER

MODELING AND SIMULATION OF THE DESULFURIZATION OF A SOUR GAS STREAMS BY ADSORPTION: INFLUENCE OF THE ISOTHERM MODEL

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ABSTRACT

The presence of elemental sulfur (S₈) in the natural gas streams has caused several problems at the delivery points, one of the most recurrent being the deposit of "yellow powder" in the pilots of pressure control valves. The presence of H₂S in the natural gas stream may serve as the source for the S₈ and/or increase the solubility thereof in the gas. Studies have shown that the adsorption control mechanisms are more attractive for use in pipelines to control S₈ deposition. In this study, computational simulations were performed in the software Comsol Multiphisics, using the Computational Fluid Dynamics (CFD) technique and 13X zeolite as adsorbent. The isotherm models of Langmuir, BET, Freundlich, Toth and Sips were tested in the modeling and simulation and the results obtained showed that the isotherm models presented the following decreasing order of precision in relation to the experimental results: Sips = Freundlich> Toth> Langmuir> BET. In addition, it was possible to verify that the variation of the coefficient of axial dispersion influences significantly the size of the mass transfer zone.

Keywords: Natural Gas; Elementar Sulfur; Desulfurization methods; Adsorption; CFD simulation.

Highlights

The presence of H_2S in the gas stream favors the deposition of S_8 in the transport of natural gas. A modeling and simulation of the removal of H_2S from the gas stream by adsorption is proposed. The Freundlich and Sips isotherm models showed the best results in the modeling and simulation. The axial dispersion coefficient is an extremely important parameter in the modeling.

INTRODUCTION

Global energy demand continues to increase, at the same time as it has become necessary to develop sustainable policies. Current concerns should be focused on how to produce sufficient energy, with high quality, economic viability and environmental sustainability. When these needs are taken into account, natural gas becomes one of the most attractive sources of fossil fuels.

Although natural gas is considered a "clean" fuel compared to other fossil fuels, the form in which it is found is not totally free of impurities. According to [1] natural gas consists mainly of methane, however, other non-hydrocarbon compounds may be present, the most common being nitrogen (N_2), carbon dioxide (CO₂), water (H_2O) and sulfur compounds, such as: hydrogen sulphide (H_2S), mercaptans (RSH), carbonyl sulfide (COS), carbon disulfide (CS₂), sulfur vapour (S) and elemental sulfur (S_8).

In the production and transport of natural gas several problems can occur, with the formation and deposition of elemental sulfur being one of the most recurrent. The formation of elemental sulfur in natural gas pipelines occurs mainly in pressure reducing pilot valves, from the Joule-Thomson effect where the deposition rate is higher [1]. Therefore, pressure drop seems to be an important parameter to describe the deposition mechanism, since a pressure reducing leads to a cooling of the gas stream. Thus, when reaching the pressure and temperature conditions below of the triple sulfur point, occurs the direct passage of the sulfur from the vapor phase to the solid phase (desublimation). The formation and deposition of S_8 in pipelines can lead to a number of problems affecting transport safety from production in the wells to the processing of natural gas [2]. According to [3], the blockage caused in the ducts by the deposition of elemental sulfur, as well as the corrosion that can be caused due to the presence of this compound can result in equipment failures that will have as consequence a reduction in the production, or even its stoppage.

The deposition of elemental sulfur in the equipment for measuring the volume of transported gas can lead to errors of up to 2%, and in more extreme cases may be even greater [4-5]. Studies performed by [6] showed that a 2% error in the measurement of marketed volume could lead to extremely significant losses of revenue when involving large volumes of transported natural gas, as well as being subject to financial sanctions by the regulator depending on the country where the company operates.

 H_2S removal from the gas stream is one of the alternatives for solving the problem of S_8 , since the presence of this compound may be the source for the formation of elemental sulfur [7]

and/or can act as a solvent increasing the natural gas's ability to charge S_8 in gas pipelines contributing to increase the desublimation downstream of the pressure drop points. [8-9]. Therefore, an interesting alternative is removal of the sulfur compounds from the gas stream before it reaches the pressure and temperature conditions that lead to the desublimation process. There are several treatment processes for desulphurisation of natural gas, among which we can mention: absorption, adsorption, oxidation, use of membranes and conversion. In the elemental sulfur problem in pipelines, S_8 is solubilized in the gas stream transported at very low levels (ppmv or even less) and, for this scenario, control mechanisms for adsorption are those that are more attractive for use in the control of elemental sulfur deposition due to the complexity of the processes and to the costs involved in implementation and maintenance [10]. Many studies have been focused on understanding of the S_8 formation mechanism [1-5] and its impacts [2, 6-7], however, studies addressing the use of adsorbents as an alternative to prevent the problem of formation and deposition of elemental sulfur in natural gas pipelines are little discussed in the literature.

The process of transporting natural gas through ducts involves high flows and pressures, which makes it difficult to reproduce the process experimentally in laboratories. However, with the advancement in the development of numerical methods the Computational Fluid Dynamics (CFD) technique has been used to predict the behavior of fluid flow, which allows an understanding of the processes on a large scale. The main objective of this work is to perform the modeling and simulation of the process of desulphurising gas streams through adsorption using 13X zeolite, since this adsorbent has been widely used in the removal of H₂S [11-12] and mercaptan [13-14]. Therefore, from the definition of the isotherm model that best represents H_2S removal by adsorption, the operational conditions of the pipelines may be better investigated using CFD technique.

METHODOLOGY

The choice of adsorption as a desulphurisation method to be used as a possible solution to the problem of S_8 was made based on previous studies [10], and the computational tool Comsol Multiphisics version 4.3a was used for modeling and simulation of the process. The choice of zeolite 13X as adsorbent is due to this product being already commercial and much used in the desulphurisation of gas streams, as already discussed, used in Sigot's work [12], because it has all the necessary parameters to predict the behavior of the adsorption column.

After choosing [12], the equilibrium parameters for the isotherm models used in this work were obtained: Langmuir, Freundlich, BET (Brunauer, Emmett and Teller), Toth and Sips. The parameters of the isothermal models were obtained through the non-linear adjustment, and the Statistica 8.0 program was used. The quasi-Newton and Hooke-Jeeves methods were used to estimate the parameters of each model. In addition, the confidence intervals of each parameter, as well as the correlation coefficient (R), were obtained by the Statisitca 8.0 program. Table 1 presents information on the adsorbent and adsorption column used as input data in Comsol.

Table 1

According to [12], the gas stream in the adsorption column feed is a mixture of CH₄ (42.7%), CO₂ (41.5%), H₂O (1.3%), O₂ (2%) in percent volume and H₂S (4060 part per million vapor) that represent a sour gas stream.

Mathematical Modeling

Mathematical modeling is one of the most important parts of a simulation. For the cases simulated the following hypotheses were assumed:

 \checkmark Transient regime, isothermal and adiabatic flow;

 \checkmark The properties of the gas are described by the Peng-Robinson state equation;

 \checkmark Constant bed properties along the flow (density, porosity, permeability and interstitial velocity);

 \checkmark The temperature and concentration gradients in the radial and angular directions are negligible;

 \checkmark The mass transfer rate is represented by the Linear Driving Force (LDF);

 \checkmark There is axial diffusion only in the Z coordinate (the bed is considered 1D);

✓ Physical adsorption.

The hypotheses assumed in this work have been widely accepted by various studies of adsorption [13-17].

In this process, the gas is almost dry and its temperature is low in the adsorption step and, therefore, the gas follows non-ideal behavior so the gas properties such as density and viscosity are obtained from Peng–Robinson equation of state [13].

The differential mass balance for an adsorbate in a fixed bed column involves axial dispersion, convective flow, fluid phase accumulation and adsorption rate, as described by Equation (1) [18]:

$$-D_{L}\frac{\partial^{2}C}{\partial z^{2}} + \upsilon\frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{(1-\varepsilon)\rho_{P}}{\varepsilon}\frac{\partial q}{\partial t} = 0$$
(1)

Where: D_L is the coefficient of axial dispersion, *C* is the concentration of the solute in the fluid phase, *z* is the length of the bed, *v* is the interstitial velocity of the fluid, *t* is the time, ε is the porosity of the bed, ρ_P is the density of the adsorbent and *q* is the concentration of the solute in the solid phase (adsorbed).

The coefficient of axial dispersion can be obtained from the correlation of Wakao-Funazkri [17], according to Equation (2):

$$\frac{\varepsilon D_L}{D_m} = \varepsilon_0 + 0.5Sc \operatorname{Re}$$
⁽²⁾

Where: ε_0 corresponds to the stagnation contribution of the axial dispersion, *Sc* is the Schmidt number, Re is the Reynolds number and D_m is the molecular diffusivity. According to [19], the stagnation term has an important effect on fixed bed dynamics and for low Reynolds numbers (Re <0.5) the value 0.23 is used, whereas for high Reynolds numbers (Re> 10) the value of 20 is used.

For the solution of Eq. (1), which describes mass transfer from the fluid phase to the solid phase, the approximation of the Linear Driving Force (LDF) is used. The LDF model assumes a linear behavior for the mass transfer along the bed, as presented in Equation (3):

$$\frac{\partial q}{\partial t} = K_s \left(q_e - q \right) \tag{3}$$

Where: K_s is the global mass transfer coefficient and q_e is the value of q in equilibrium with C.

The LDF mass transfer model described is assumed to be a linear function of the solid. In this way, the global mass transfer coefficient involves the extra particle transport mechanism and another of intraparticle transport, being composed of two terms as described in Equation (4) [18]:

$$\frac{1}{K_{s}} = \frac{d_{p}q_{0}\rho_{b}}{6k_{e}c_{0}\varepsilon} + \frac{d_{p}^{2}q_{0}\rho_{b}}{60D_{e}c_{0}\varepsilon}$$
(4)

Where: d_p is the particle diameter, q_0 is the value of q (concentration in the solid phase) in equilibrium, ρ_b is the density of the bed, k_g is the coefficient of external mass transport, c_0 is the contraction of H₂S in the supply and D_e is the effective diffusivity.

The external mass transfer coefficient is estimated from the Sherwood number (*Sh*) and the Wakao-Funazkri correlation [17], according to Equation (5) and (6):

$$Sh = 2 + 1.1Sc^{\frac{1}{3}} \text{Re}^{0.6}$$
 (5)

$$k_g = \frac{ShD_m}{d_p} \tag{6}$$

The molecular diffusivity can be obtained from the Fuller-Schettler-Gridding correlation [20], according to Equation (7):

$$D_{m} = \frac{10^{-3} T^{1.75} \left(\frac{1}{MM_{gas}} + \frac{1}{MM_{H_{2}s}} \right)^{0.5}}{P \left(V_{gas}^{\frac{1}{3}} + V_{H_{2}s}^{\frac{1}{3}} \right)^{2}}$$
(7)

Where: *T* is the temperature, MM_{gas} is the molecular mass of the gas, MM_{H2S} is the molecular mass of H₂S, *P* is the pressure, V_{gas} is the diffusion volume of the gas and V_{H2S} is the diffusion volume of H₂S.

The effective diffusivity in the macropores was calculated with the Bosanquet equation (Equation 8) [13, 19]:

$$\frac{1}{D_e} = \tau_p \left[\frac{1}{D_m} + \frac{1}{D_K} \right]$$
(8)

Where: τ_p is the tortuosity factor of the particle and D_K is the Knudsen diffusivity.

The Knudsen diffusivity and the tortuosity factor of the particle can be obtained from Equations (9) and (10) [17]:

$$D_{K} = 97r_{poro} \left(\frac{T}{MM_{H_{s}S}}\right)^{0.5}$$
(9)

$$\tau_p = \varepsilon_p + 1.5(1 - \varepsilon_p) \tag{10}$$

Where: r_{pore} is the radius of the pore, *T* is the temperature and ε_p is the porosity of the particle.

For the modeling and simulation in the case studied the coefficient form PDE interface was added using the partial differential equations (PDE) module, which is dependent on time and onedimensional flow. To solve the model implemented this software uses the Finite Element Method to numerically solve the differential equations using the variable u, as shown in Equation (11):

$$e_{a}\frac{\partial^{2}u}{\partial t^{2}} + d_{a}\frac{\partial u}{\partial t} + \nabla\left(-c\nabla u - \alpha u + \gamma\right) + \beta\nabla u + au = f$$
(11)

Where: e_a is the mass coefficient, d_a is the damping or mass coefficient, c is the diffusion coefficient, α is the conservative flow convection coefficient, γ is the conservative flow source term, β is the convection coefficient, a is the sorption coefficient and f is the source term.

In order to be able to use the coefficient form PDE it is necessary to make Eqs. (1) and (3) dimensionless for concentration, adsorbed amount, time and length. For this, we use Equations (12) to (15):

$$x = \frac{c}{c_0} \tag{12}$$

$$y = \frac{q}{q_0} \tag{13}$$

$$\tau = \frac{t\upsilon}{L} \tag{14}$$

$$l = \frac{z}{L} \tag{15}$$

Where: x is dimensionless concentration of H_2S in gas phase, y is dimensionless concentration of H_2S in solid phase, τ is the dimensionless time, v is the interstitial velocity, *l* is the dimensionless length and *L* is the length of the bed.

Substituting Eqs. (12) to (15) into Eqs. (1) and (3), as well as making some mathematical simplifications results in Equations (16) and (17):

$$-\frac{D_L}{L\nu}\frac{\partial^2 x}{\partial l^2} + \frac{\partial x}{\partial l} + \frac{\partial x}{\partial \tau} + \frac{(1-\varepsilon)\rho_p q_0}{\varepsilon c_0}\frac{\partial y}{\partial \tau} = 0$$
(16)

$$\frac{\partial y}{\partial \tau} = \frac{k_s L}{\upsilon} \left(y^* - y \right) \tag{17}$$

Where: y* corresponds to the isothermal models described above.

From Eqs. (16) and (17) it is possible to obtain some dimensionless variables that will be implemented in the PDE coefficient form, as can be seen from Equations (18) to (20):

$$P_e = \frac{\upsilon L}{D_L} \tag{18}$$

$$D_g = \frac{(1-\varepsilon)\rho_p q_0}{\varepsilon c_0} \tag{19}$$

$$S = \frac{k_s L}{\nu} \tag{20}$$

Where: P_e is the Peclet number, D_g is called the distribution coefficient and S is the dimensionless global mass transfer coefficient.

For Eqs. (16) and (17) to be solved it is necessary to add two coefficient form PDE interfaces, since the additional variables defined, *x* and *y* represent different physical quantities. The solution is found in the coefficient form PDE 1 interface considering x = u1, and the coefficients are as follows:

$$e_a = (0), d_a = (D_g), c = (1/P_e), \alpha = (-1), \gamma = (0), \beta = (0), a = (0) \text{ and } f = (0)$$

The solution is found in the coefficient form PDE 2 interface considering y=u2, and the coefficients are as follows:

$$e_a = (0), d_a = (0), c = (0), \alpha = (0), \gamma = (0), \beta = (0), a = (S) \text{ and } f = (y^*)$$

To solve the problem it is necessary to define the initial and boundary conditions. In this case, these conditions are described by Equation (21):

$$\tau = 0, x = 0, y = 0 (0 \le l \le 1)$$

$$l = 0, x = 1, (\tau > 0)$$

$$l = 1, \frac{\partial x}{\partial l} = 0, (\tau > 0)$$
(21)

In order that the conditions described by Eq. (21) can be added in each coefficient form PDE interface it is necessary to add two new boundary conditions: Dirichlet type for l=0 (u = r) and Flux-Source type for l=1 ($-n(-c\nabla u - \alpha u + \gamma) = g - q_a u$). For the coefficient form PDE 1 interface the boundary conditions are:

$$r = (1), q_a = (1) \text{ and } g = (0)$$

For the coefficient form PDE 2 interface the boundary conditions are:

$$r = (0), q_a = (0) \text{ and } g = (0)$$

The next step is the simulation processing through the use of the solver tool which consists of applying the Finite Element Method for each discretized control element to the equations until the desired convergence occurs. In this step the time increment can also be set. After an optimization study, a dimensionless time step of 10 and a mesh with 5000 triangular elements were used. The relative tolerance used was equal to 10^{-4} .

The results obtained from the simulations were compared with the experimental data through numerical error analysis. This becomes necessary because the use of numerical methods works with approximate values of the results of the partial derivatives, which can lead to a difference between the predicted values and the experimental values. The value of the average relative error between the experimental and predicted results can be obtained from Equation (22).

$$ERM = \sum \frac{\left(\frac{E-P}{E}\right)}{n}$$
(22)

Where: E is the experimental value, P is the predicted value and n is the number of experimental and predicted points.

RESULTS AND DISCUSSION

Determination of the equilibrium parameters

The equilibrium parameters for the isotherm models (Langmuir, Freundlich, BET, Toth and Sips) were obtained from the experimental data of [12]. The experimental data of the rupture curve (Figure 1) obtained by [12] for the adsorption of H_2S in zeolite 13X were used to obtain the parameters of the isothermal models.

Figure 1

From Figure 1 it is possible to verify that the rupture that corresponds to the time that the H₂S is detected at the output occurred after 20 h, and according to the authors the recorded value was 1 ppmv ($C/C_0=2.46 \times 10^{-4}$). The exhaustion of the bed occurred after 50 h and the rupture curve showed values of C/C_0 greater than 1. According to [12], this is due to the fact that the study was carried out in the field and variations in the H₂S content in the occurred feed stream during the experiments, with minimum, average and maximum values being 3585 ppmv (0.139 mol / m³), 4060 ppmv (0.158 mol / m³) and 4460 ppmv (0.173 mol / m³), respectively. Figure 2 shows the adjustment of the equilibrium data for the different isotherm models.

Figure 2

From Figure 2 it is possible to verify that the isotherm models fitted satisfactorily to the experimental data. However, the Langmuir and BET models presented the greatest discrepancy, especially at low concentrations, while the Freundlich and Sips models were the best fit for the experimental values and is confirmed based on the correlation coefficient R in Table 2. The values of the parameters were obtained for the models with the respective confidence intervals (with 95% confidence). In Table 2, q_s represents the maximum amount adsorbed by the model, B is the constant of the isotherm model, n the exponent of the model and b_L is the equilibrium constant between the solute and the layer of the adsorbed molecules in the BET model.

Table 2

From Table 2 it is possible to verify the confidence intervals of the parameters of each model, except for the Toth and Sips models. This is common when the model has parameters with no statistical significance, and it is common to not be able to invert the parametric sensitivity matrix in these cases. In the other models in which it was possible to calculate the reliable intervals of the parameters, it is observed that all have significant parameters with 95% confidence, because when

the reliable interval of the parameter is greater than the value of the parameter, it has no statistical significance and can be removed from the model [21]. It is worth mentioning that great care must be taken when selecting models only by the correlation coefficient (R), since the Freundlich and Sips models, although presenting the best fit may have parameters with no statistical significance. In addition, the correlation coefficient between the two models was the same. However, the Freundlich model gives the same result but with one parameter less.

Table 3 shows the adsorption data and mass transfer parameters for each isothermal model. The required parameters that were kept constant for each isotherm model are: external mass transfer coefficient (k_g), amount adsorbed at equilibrium (q_0), global mass transfer coefficient (K_s), dimensionless mass transfer coefficient (S) and distribution coefficient (Dg).

Table 3

Influence of the isotherm model and axial dispersion coefficient

From the parameters obtained for each isotherm model it was possible to obtain their respective rupture curves. To verify if the simulations are consistently representing the adsorption of H_2S in the 13X zeolite it is necessary to compare the simulated and experimental breakthrough curves obtained by [12].

As discussed in the methodology, the stagnation term that involves the calculation of the coefficient of axial dispersion (Eq. 2) has an important effect on the dynamics of the fixed bed and, therefore, its influence on the rupture curves was also evaluated in this section. In the case under study, the Reynolds number calculated (Re = 3.69) is in the transition zone between what [19] ranks as low Reynolds number (Re <0.5) and high Reynolds numbers (Re> 10). Thus, using Equation 2, we determined the values of the axial dispersion coefficient considering the stagnation term (ε_0) equal to 0.23, 2, 10 and 20, which resulted in dispersion coefficient values 6.57x10⁻⁵ m²/s, 1.49x10⁻⁴ m²/s, 5.27x10⁻⁴ m²/s and 9.98x10⁻⁴ m²/s, respectively. Therefore, in order to verify the influence of the isotherm model and the axial dispersion coefficient in each isotherm model, this parameter was varied in the simulations and the others were kept constant. Figures 3 shows the results obtained using the Langmuir isotherm model.

Figure 3

From Figure 3 it is possible to verify that the value of the stagnation term and, consequently, the calculated axial dispersion coefficient significantly influenced the results. The variation of the coefficient of axial dispersion from 6.57×10^{-5} to 9.98×10^{-4} m² / s caused the Peclet

number to vary from 54.8 to 3.61 and, consequently, displaced the point of rupture to the left causing a saturation of the bed to occur in a shorter time. According to [18], this is due to the increase of the axial dispersion causing the flow pattern to deviate from the ideal plug flow model. Therefore, the effect of the axial dispersion becomes undesirable since its increase leads to a reduction in the efficiency of the porous bed and, consequently, its saturation occurs more quickly. Thus, in the case studied, the results show that the mass transfer zone is strongly influenced by the effects of axial dispersion. In addition, the choice of a suitable value for the stagnation term that was within the range of low Reynolds numbers (ε_0 =0.23) allowed a better fit between the experimental and the simulated curve.

From Figure 3 it is possible to verify that the Langmuir isotherm model using a suitable axial dispersion coefficient value was able to predict a break point close to the experimental one even though it had a low correlation coefficient value (R = 0.68) in the adjustment of the equilibrium data. However, when a quantitative analysis was performed, the predicted value after 20 h was $C/C_0=7.87 \times 10^{-4}$, whereas, according to [12], the concentration at the exit after 20 h reached 1 ppmv ($C/C_0=2.46 \times 10^{-4}$), which represents a relative error of 219.9%. Thus, the Langmuir model was not able to accurately predict the break point. After 50 h, time obtained for bed exhaustion by [12], in the conduction of the experiments, the simulated curve presented a maximum relative error point of 10.1% and an average relative error of 7.04%, and the highest relative errors were obtained where the experimental curve presented values greater than 1. This occurs due to variations in the content of H₂S in the content of in the feed stream, a phenomenon which can not be considered by the simulated curve considering a feed current with constant contaminant content (0.158 mol/m³).

It is noteworthy that the study by [12] was in the field which makes it more complicated to control the variables involved in the process and, according to the author, the uncertainties in the measurements of the H_2S content may vary from 10% to 20%. Therefore, the results obtained by the Langmuir model in predicting bed depletion can be considered unsatisfactory.

Figure 4 shows the analysis for the BET isotherm model by varying the coefficient of axial dispersion.

Figure 4

From Figure 4 it is possible to verify that the behavior of the rupture curve predicted by the BET model was similar to the results obtained by the Langmuir model. As the coefficient of axial

dispersion increased, the rupture curve shifted to the left, which causes the break point to occur in a shorter time. As already discussed for the Langmuir model, this is due to the fact that the amplitude of the mass transfer zone is governed by the axial dispersion. The best fit between the simulated and the experimental curves occurred when using a value of 0.23 for the stagnation term. However, the rupture point in the simulated curve only occurred after 25 h, as well as failed to predict the behavior of the rupture curve over its entire length since it has a greater slope when compared to the experimental one. The predicted value after 20 h (experimental rupture time) was $C/C_0= 7.16 \times 10^{-9}$, which represented a relative error of approximately 100% when compared to the experimental value that was $C/C_0= 2.46 \times 10^{-4}$, while from 50 h the maximum relative error was 13.1% and the average relative error was 9.57%. Thus this isotherm model was not shown to predict the rupture time or the complete rupture curve.

Figure 5 shows the evaluation for the Freundlich isotherm model by varying the axial dispersion coefficient.

Figure 5

From Figure 5 it is possible to verify that simulated curves show a similar behavior to the previous models, that is, the variation of the of axial dispersion coefficient of 9.98×10^{-4} up to 6.57×10^{-5} m² / s causes a shift of the rupture curve to the right. This causes the simulated curves to approach the experimental curve obtained by [12] as the value of the axial scattering coefficient decreases. Regarding the shape of the rupture curve, it is possible to verify that the Freundlich model was able to predict a greater approximation of the experimental rupture curve in all its extension for the smaller value of axial dispersion. After 20 h the value predicted at the rupture was $C/C_0= 2.68 \times 10^{-4}$, which represents a relative error of 8.94% when compared to the experimental value 2.46 $\times 10^{-4}$. Considering the variation in feed concentration discussed earlier, this isotherm model was able to predict well the moment the contaminant begins to be detected at the exit of the adsorption column. In relation to bed exhaustion, the maximum relative error was 6.06% and the average relative error was 4.1%. Thus, the Freundlich isotherm model proved to be satisfactory both in obtaining the rupture time and in predicting the adsorption column exhaustion time.

Figure 6 shows the results obtained with the use of the Toth model. Again, the results showed a behavior similar to the previous models, since a reduction in the dispersion coefficient reduced the mass transfer and shifted the rupture curve to the right. The best fit between the simulated and experimental results occurred for the value of D_L equal to 6.57×10^{-5} m²/s based on the greater approximation between experimental and simulated rupture curves.

As for the rupture time, after 20 h the simulated value for the rupture curve was C/C_0 = 4.71x10⁻⁴ and, therefore, this value represents a relative error of 91.5%. Therefore, the Toth model was not able to predict satisfactorily the time that H₂S starts to be detected at the adsorption column output, however, from 50 h, the maximum relative point error was 4.04% and the average relative error was 3.56%, which is lower than that obtained for the Freundlich adsorption model (4.1%). Thus, considering the time for exhaustion of the bed, the Toth model was able to predict the rupture curve satisfactorily.

The last model to be evaluated was the Sips isotherm model. This model is interesting because it combines the Langmuir and Freundlich isotherm models, which are those traditionally most used to predict the behavior of adsorption studies. The results for the Sips isotherm model are shown in Figure 7.

Figure 7

From Figure 7 it is possible to observe the same behavior obtained for the other isotherm models studied. The reduction of the axial dispersion coefficient caused a decrease in the mass transfer, which made the simulated curves close to the experimental one. As in the other models, the best fit between the experimental and simulated curve occurred for the axial dispersion coefficient equal to 6.57×10^{-5} m²/s. The simulated value after 20 h was $C/C_0 = 2.58 \times 10^{-4}$ and therefore a relative error equal to 4.87% was obtained when compared to the experimental value. Thus, the Sips model was able to predict satisfactorily the moment the contaminant begins to be detected at the exit. The maximum relative error and the average error obtained after 50 h were 5.05% and 3.88%, respectively. Thus, the Sips isotherm model was the one that was able to predict with less error (less than 5%) both the time of rupture and the exhaustion of the bed.

In order to make a better analysis of the results, Figure 8 shows the comparison between the different isotherm models with the dispersion coefficient equal to 6.57×10^{-5} and the experimental curve of [12].

Figure 8

From Figure 8 it is possible to verify the superiority of the other models in relation to the BET model, since this one presents the greatest discrepancy in relation to the experimental curve. The rupture curves obtained with the Freundlich and Sips isotherm model were overlapped, which shows that either of them can be used in the prediction of the rupture curve, while the Toth model presented intermediate results. Thus, based on Figure 8, the classification of the models used in the prediction of the H₂S rupture curves in zeolite 13X in order of approximation with respect to the experimental results were: Sips = Freundlich> Toth> Langmuir> BET. It is worth mentioning that the Freundlich model is a two-parameter model while the Sips model is of three parameters which

shows that the inclusion of one more parameter does not bring significant increments in the results, that is, from the statistical point of view this parameter additional has no significance, which makes the Freundlich model easier to use in this case. Another important point is that the rupture curves help confirm what has been discussed previously regarding the care one should take in choosing models taking into account only the correlation coefficient. As was seen in the cases studied, a model with a lower R value, Langmuir, achieved a better approximation with the experimental curve when compared to the BET model that had a value of R = 0.94.

As previously discussed, 13X zeolite presents potential for the removal of different sulfur compounds from gas streams and, therefore, could be used to remove H₂S from natural gas, since this compound favors the formation and deposition of S₈. Another advantage of using this adsorbent as a methodology to mitigate S₈ problem is that the 13X zeolite has the ability to be regenerated allowing its used in more than one adsorption cycle. The regeneration of the 13X zeolite can be performed by Pressure-Temperature Swing Adsorption (PTSA) process [13] or by high temperature desorption at 500–600 °C in inert atmosphere or by desorption–oxidation in air at a temperature <400 °C, conform proposed by [22]. Therefore, 13X zeolite shows technical feasibility, as it has good adsorption cycle, to be used as a methodology to mitigate the formation and deposition problem of S₈.

CONCLUSIONS

In this work a modeling and simulation of the process of desulphurisation of gas currents using the adsorption technique was carried out. From the obtained results it was possible to conclude that the mathematical modeling was able to predict the behavior of the H₂S curve in zeolite 13X and among the isotherm models used it was possible to verify the superiority of the Freundlich and Sips models in relation to the others, both in determining the rupture point and the bed exhaustion. In addition, it is possible to conclude that the value of the correlation coefficient can not be the only parameter to be taken into account to choose the best isotherm model. It was possible to verify that the axial dispersion is a parameter that significantly influences the size of the mass transfer zone and, consequently, the saturation time of the bed. The choice of the best isotherm model and an adequate axial dispersion coefficient allowed a good approximation between the simulated curve and the experimental curve of [12] allowing a validation in the simulated results.

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Figure captions:

Figure 1 - Experimental data for 13X zeolite adsorption at 25 °C. Modified of [12].

Figure 2 - Comparison between the experimental equilibrium and predicted data by the different isotherm models.

Figure 3 - Comparison between the experimental and simulated rupture curve using the Langmuir model for different axial dispersion coefficients.

Figure 4 - Comparison between the experimental and simulated rupture curve using the BET model.

Figure 5 - Comparison between the experimental and simulated rupture curve using the Freundlich model.

Figure 6 - Comparison between the experimental and simulated rupture curve using the Toth model.

Figure 7 - Comparison between the experimental and simulated rupture curve using the Sips model.

Figure 8 - Comparison between simulated and experimental data for the different isotherm models.

Adsorbate	H_2S	
Concentration of H_2S in the feed (mol/m ³)	0.158	
Adsorbent	Zeolite 13X	
Bed length (mm)	100	
Diameter of bed (mm)	40	
Particle Diameter	2	
Particle Density (kg/m ³)	1100*	
Particle Porosity [-]	0.24*	
Average pore diameter (m)	9.5x10 ⁻¹⁰	
Density of bed (kg/m ³)	700	
Porosity of bed [-]	0.36	
Feed rate (L/min)	1	
Pressure (bar)	1	
Temperature (K)	298	

Table 1 - Adsorbent and adsorption column of [12].

*Taken from [13].

qs (mol/kg)	В	n	bl	R
3.96±0.08	3472.93±2292.10	-	-	0.68
-	4.92±0.04	0.087 ± 0.002	-	0.99
6.03	6.57×10^7	0.17	-	0.97
2.04	2.41	0.087	-	0.99
3.51±0.08	6720.47±2551.98	-	1.07±0.16	0.94
	qs (mol/kg) 3.96±0.08 - 6.03 2.04 3.51±0.08	qs (mol/kg) B 3.96±0.08 3472.93±2292.10 - 4.92±0.04 6.03 6.57x10 ⁷ 2.04 2.41 3.51±0.08 6720.47±2551.98	qs (mol/kg) B n 3.96±0.08 3472.93±2292.10 - - 4.92±0.04 0.087±0.002 6.03 6.57x10 ⁷ 0.17 2.04 2.41 0.087 3.51±0.08 6720.47±2551.98 -	qs (mol/kg) B n bL 3.96±0.08 3472.93±2292.10 - - - 4.92±0.04 0.087±0.002 - 6.03 6.57x10 ⁷ 0.17 - 2.04 2.41 0.087 - 3.51±0.08 6720.47±2551.98 - 1.07±0.16

Table 2 - Balance parameters for the different isotherm models.

Parameters	k _g (m / s)	q _s (mol / kg)	$\mathbf{K}_{\mathbf{s}}\left(\mathbf{s}^{-1}\right)$	S	\mathbf{D}_{g}
Langmuir	0.034	3.95	3.16x10 ⁻⁵	8.78x10 ⁻⁵	4.86x10 ⁴
Freundlich	0.034	4.17	2.99x10 ⁻⁵	8.30x10 ⁻⁵	5.13x10 ⁴
BET	0.034	4.23	2.95x10 ⁻⁵	8.19x10 ⁻⁵	5.20x10 ⁴
Toth	0.034	4.06	3.07x10 ⁻⁵	8.52x10 ⁻⁵	4.90x10 ⁴
Sips	0.034	4.18	2.98x10 ⁻⁵	8.29x10 ⁻⁵	5.14x10 ⁴

Table 3 - Parameters of adsorption and mass transfer used in the simulations.



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8