

Simulation study on sulfur removal from algerian natural gas using adsorption on high density polyethylene membrane

A.I. Hammou^{1*}, C. Harrats², M. Djennad¹

¹Process Engineering Department, Faculty of Sciences and Technology, University Abdelhamid Ibn Badis of Mostaganem, BP/227, Mostaganem, 27000, Algeria.

²Laboratory of Applied Chemistry (LAC), DGRSDT, Ctr. Univ. Bouchaib Belhadj Ain Temouchent BP/284, 46000 Ain Temouchent, Algeria.

*Corresponding author: abdelillah.hammou@univ-mosta.dz; Tel.: +213 550 557 389 or +213 659 498 624.

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ABSTRACT/RESUME

Abstract: A simulation study was carried out on the use of tubular membrane for the capture of H₂S from Algerian liquefied natural gas. A bed composed of dense microporous membranar particles of high density polyethylene was considered. Almeesoft simulator integrating Hysis membrane calculation was employed. A clogging time of 53 minutes, adsorption capacity of 2924 mg/g and a transmembranar pressure of 0.37 bars were calculated. Furthermore, the selectivity, the maximal gas pressure, the maximal natural gas concentration and the adsorption models were considered. Particular focus was put on the permeability between the membrane skin and the natural gas.

I. Introduction

The gas emissions issued from the various industries constitute nowadays a great concern for both governments and international organizations for the environment protection. The most important sources of gaseous pollutants remain the oil and the associated petrochemical industries [1, 2]. To preserve the environment and improve the public health a huge effort is continuously made both on legal and technical levels. The former allows, via legal standards, to constrain polluters to include the pollution issues in any market development, whereas, the later investigate the possible scientific and technical approaches to reduce the emissions and/or to neutralize their negative effects. So far, many methods are considered in the treatment of the gas emissions including adsorption, condensation and absorption with or without chemical reactions [3].

Among these and although expensive chemically reacting the toxic species to neutralize them from the emitted gases is the most efficient method. Hydrogen sulfide is one of these toxic gases that the concentration of which has to be reduced to permitted level from natural gas. Governments and international organizations including the United Nations have strongly stressed companies to reduce the content of sulfur in the natural gas prior to end

use. Various limits were fixed during the past two decades depending on the countries rules and on the areas where the gases are consumed, i.e. seas, lands or cities. A close survey of the environment literature reveals that the removal of the hydrogen sulfide from natural gas is largely investigated in the area of air depollution. This gas contaminant becomes weakly acidic in the presence of water traces. Consequently it causes corrosion to the equipments, pollutes the environment and has dramatic consequences on the public health [4, 5]. The desulfurization of natural gas is a crucial phase in the gas processing industries. Note that a large volume of the world reserves of natural gas is not economically competitive because their high sulfur content exceeds 0.4 % of sulfur [6]. Many methods have been developed for the desulfurization of natural gas, including chemical neutralization and physical removal via adsorption on microporous bed of char coal. The ultimate target of these techniques is the fixation or the isolation of a maximum amount of H₂S from the natural gas. The technology of adsorption using membranes has progressed very fast to become a promising alternative to the chemical reaction classically used to trap H₂S molecules from natural gas. Inorganic and organic polymer based membranes were used in the form of a bed of solid microporous particles [7].

In addition to the limited experimental research work published on the reduction of sulfur content from natural gas, simulation was recently potentially considered for the same purpose. This is mainly motivated by the safety risks exposed to when conducting laboratory experimental research on H₂S transport properties. Chengzhen et al. realized an interesting simulation work on the removal of H₂S and CO₂ from methane using graphene membrane [8]. The concept of large scale atomic molecular massively parallel simulator (lammmps) was employed. The graphene membrane having an appropriate pore size and geometry could reach a high degree of selectivity and permeation for the separation of methane and hydrogen sulfide gases. The gas permeation was found to depend strongly on the adsorption on the graphene membrane surface. The authors observed a competitive adsorption mechanism on the graphene surface between the components of the gas mixture. A non uniform distribution of the molecules was deduced due to permeation through the nanopores. To study the adsorption selectivity of sulfur containing molecules such as H₂S and SO₂ a zirconium based metal-organic framework membrane was used [9]. It consists of the desulfurization of the mixed gases using functionalized materials UiO-66 (Zr) and UiO-66-COOH. When the membrane was functionalized using carboxyl groups a greater adsorption performance was depicted. The effect was assigned to the strong interactions induced between the sulfur molecules and the carboxyl groups attached to the membrane.

In this work, a simulation work on the elimination of a maximum amount of hydrogen sulfide from natural gas using tubular high density polyethylene membrane. Almesoft software-Hysis simulator was used to carry out the calculations. The approach was based on the theory of mono film using Langmuir and Elovich models.

II. Results and discussion

The characteristics of the membrane, its module and the working conditions used for the calculations carried out are listed in table 1.

Table 1. Characteristics of the membrane, its module and the working conditions used.

Membrane Data	
parameter	data
Bundle outer diameter (m)	0.203
Extraction tube outer diameter (d _{out}) (m)	0.051
Active bundle length (m)	5.08
Length of tube covered by holes (m)	5.08
Membrane area per module (m ²)	0.8
Inner diameter of extraction tube (d _{int}) (m)	0.05
Hole diameter (m)	0.0063
Number of holes (m)	50.8
Hole pressure drop coefficient	10 ⁴
Module Data	
name	data
external diameter (m)	0.762 10 ⁻³
Internal diameter (m)	0.635 10 ⁻³
Fiber length (m)	1.905
Pot length (m)	0.101
The working conditions	
parameter	data
The Fugacity	ideal
Feeding Pressure (atm)	30
Temperature (°C)	25
Feeding Flow Rate (m ³ .h ⁻¹)	0.05
low pressure permeate (atm)	0.7

From a HDPE polymer having a density of 0.960 g/cm³ the calculated mass (m) and volume (V_m) of a membrane having a thickness of 0.5 mm are 386.88 g and 403 cm³, respectively. A gas volume (V_g) of 9.97 liter necessary to saturate the internal membrane volume was calculated from the product of the internal surface area and the length of the tubular membrane.

II.1. Adsorption Kinetics

The kinetics of adsorption enables us to determine the contact time before equilibrium is reached and the average fluid velocity. Indeed, by fixing the volumetric flow rate and neglecting any parasite flow the variation of the pressure as a function of time is according to S. Cassette [10]:

$$P_0 = P \exp[-(D_v \cdot t) / V_g] \quad (1)$$

Where t is the contact time, V_g is the gas volume, D_v is the gas volumetric flow, P is the gas feed pressure and P₀ is the gas permeate pressure.

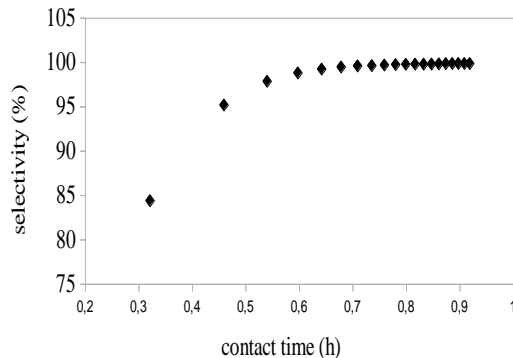


Figure 1. Effect of contact time on the selectivity of the HDPE membrane.

At room temperature and a low pressure permeate of 0.7 atm., the adsorption process has substantially and rapidly progressed as indicated by the selectivity versus time (fig.1).

A selective removal of H₂S of 98.5 % is reached after 36 min of contact time. This fast adsorption process was expected as the pores of the membrane initially empty and were progressively saturated. This is indicated by the slow increase of the selectivity within the time range of 36-53 min. Contact times larger than 53 minutes showed no change in the selectivity. It was stabilized at a value of 99.88 %. This can be explained by the expected pores saturation with H₂S molecules. If the feed pressure is greater than the permeate pressure then an average fluid velocity of about 0.025 m h⁻¹ is obtained from $U_m = D_v/A$; Where U_m is the average fluid velocity, D_v is the volumetric flow rate and A is the membrane surface.

II.2. Adsorption Isotherm

Below a feed pressure of 13.6 atm. the selectivity increased sharply to reach a value of 98.82 %. It slowed down to reach a plateau at 99.88% corresponding to a feed pressure of 57.8 atm about 58 atm. At this stage all the pores were occupied and the membrane no longer retains the H₂S molecules (fig.1).

If we consider the gas mixture as ideal gas then we can write the H₂S concentration as:

$$C = P/(R.T) \quad (2)$$

The equations 2 and 7 were used to calculate the selectivity as a function of feed, permeate and retentate concentrations, respectively. From figure 2 we deduce at equilibrium a selectivity of 99.88%, a feed concentration of 59.1 g/l, a permeate concentration of 59.07 g/l and a retentate concentration as small as 0.071g/l.

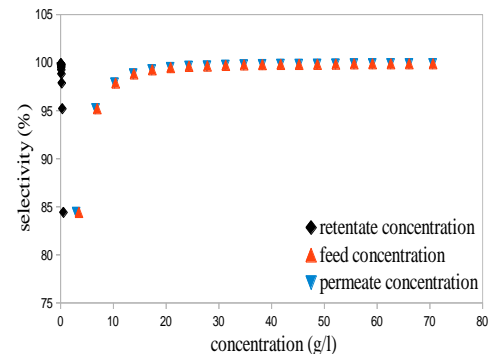


Figure 2. Effect of concentrations on the membrane selectivity.

Figure 3 shows the selectivity as a function of the permeate low pressure. The selectivity decreases in a monotonic way as permeate low pressure increases due to saturation of membrane pores. This clogging phenomenon restrains the H₂S molecules mobility in the membrane.

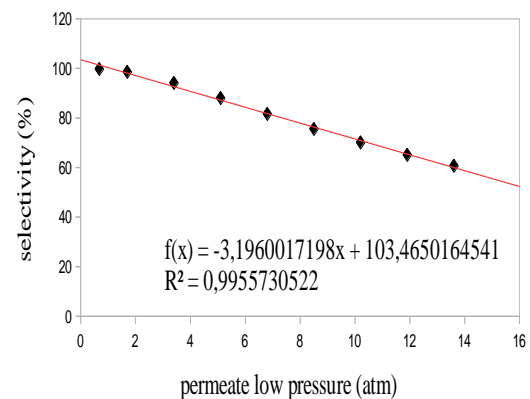


Figure 3. Effect of permeate low pressure on the selectivity of the membrane.

The effect of temperature on the selectivity is carried out at a feed pressure of 30 atm. and a permeate low pressure of 0.7 atm. The selectivity decreased linearly as function of temperature. This behavior was expected as the pores get larger due to thermal treatment. In practice this phenomenon has been ascribed to rupture of the secondary chemical bonds within the membrane (fig.4) [11].

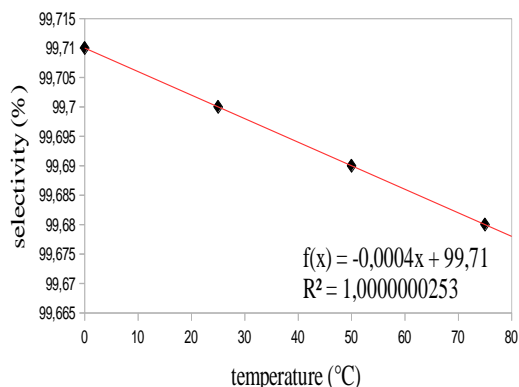


Figure 4. Effect of temperature on the membrane selectivity.

II.3. Energies Associated With the Adsorption Process

The working conditions used for the calculations carried out are shown in table 2.

Table 2. The working conditions used.

T (°C)	Permeate low Pressure P ₀ (atm)	Feed Pressure P (atm)
0	0.7	30
25	0.7	30
50	0.7	30
75	0.7	30

The distribution coefficient K_d characterizing the solute affinity for the adsorbent can be translated in equation form as:

$$K_d = (C_i/C_e) \cdot (V_g/m) \quad (3)$$

Where C_i and C_e are the initial and residual solute concentrations in (mg/l) at equilibrium, m (gr) is the adsorbent mass and V_g (ml) is the gas volume [12]. The free energy ΔG , the enthalpy ΔH and the entropy ΔS of H_2S adsorption on the membrane can be calculated using equation 4 which was derived from equation 3.

$$\ln K_d = (\Delta S / R) - (\Delta H / RT) \quad (4)$$

Where R is the molar gas constant and T (k) is the temperature [13].

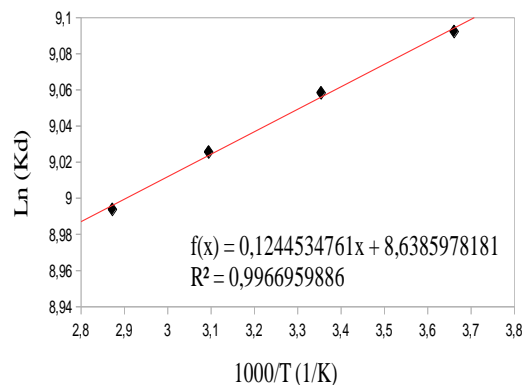


Figure 5. Effect of temperature on the sorption of H_2S by the membrane.

The plot of $\ln(K_d)$ versus $1000/T$ gives a straight line with the slope and intercept corresponding to $(-\Delta H/R)$ and $(\Delta S/R)$, respectively (Fig.5). In table 3 are listed the thermodynamic parameters calculated using the the free enthalpy $\Delta G = \Delta H - T\Delta S$ [14].

Table 3. Calculated thermodynamic parameters.

ΔS^0 (J/mol.K)	ΔH^0 (KJ/mol)	ΔG^0 (KJ/mol)			
		273.15 K	298.15 K	323.15 K	348.15 K
71.787	-1.034	-20.64	-22.447	-24.232	-26.026

- The negative value of ΔG indicates that the process of H_2S molecules elimination is spontaneous and their adsorption by the membrane is favorable.
- The negative ΔH reveals that the process is exothermic.
- $\Delta H < 40$ KJ/mol reveals that the process of H_2S fixation to the membrane is probably a physisorption phenomenon.

II.4. Adsorption Isotherm Models

Many authors have proposed theoretical models or empirical ones for the description of the relation between the adsorbate mass fixed at equilibrium (q_e) at the corresponding concentration (C_e). The amount of adsorbed solute at equilibrium is given by:

$$q_e = (C_i - C_e) \cdot (V_g/m) = \xi \cdot C_e \quad (5)$$

Where ξ is the selectivity, V_g (L) is the gas, m (g) is the adsorbate mass and C_e (mg/L) is the adsorbate concentration at equilibrium [15].

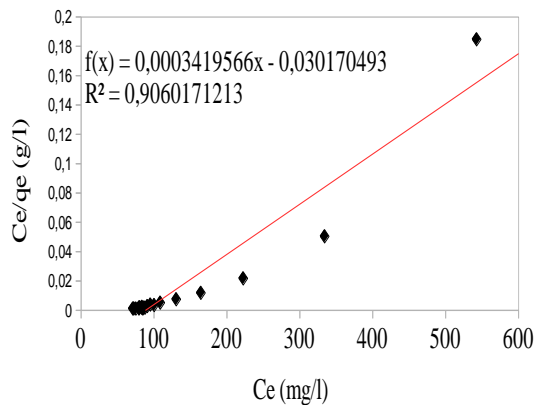


Figure 6. Langmuir adsorption isotherm of H₂S by the membrane.

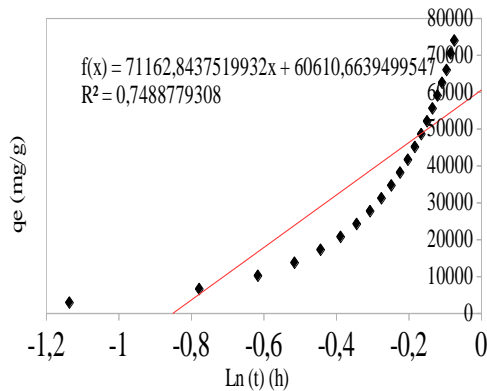


Figure 7. Isotherm according to Elovich model.

In figures 6 and 7 are plotted the adsorption isotherms according to the models of Langmuir and Elovich, respectively. The calculated data used are listed in Table 4. The results confirm that Langmuir model is the most appropriate to fit our adsorption study of H₂S molecules. A regression of 0.9 with an adsorption capacity of 2924 mg/g was found.

Table 4. Calculated parameters of Langmuir and Elovich models applied to the sorption of H₂S molecules by the membrane.

	Langmuir			Elovich		
	q_{max} (mg/g)	k (g/mg)	R^2	α (mg.g ⁻¹ .h ⁻¹)	B (g.mg ⁻¹)	R^2
H ₂ S	2924	-0.011	0.9	1.67 10 ⁵	1.405 10 ⁻⁵	0.74

II.5. Intra Particulate Diffusion Process

The kinetics of intra particulate diffusion is usually presented by: [16]

$$q_t = K_{id}.t^{1/2} + C \quad (6)$$

Where K_{id} is the rate constant of intra particulate diffusion and C is a constant. A plot of $q_t = f(t^{1/2})$ is displayed in figure 8.

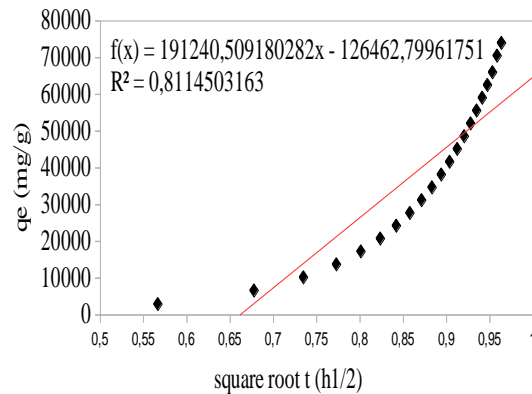


Figure 8. Intra-particulate diffusion of H₂S molecules by the membrane.

A rate constant of intra particulate diffusion K_{id} of 19.12 10⁴ mg.g⁻¹.h^{-1/2} and a constant C equal to -12.64 10⁴ mg.g⁻¹ were derived from the slope and intercept, respectively.

II.6. Membrane Clogging

Clogging is a bedding process of filtration and permeation on membranes. The formation of matter in dispersed form on the surface of the membrane leads to a reduction of the permeation process. This is due to the saturation of the membrane pores.

In figure 9 is plotted the flux of gas crossing the membrane as a function of the transmembranar pressure (TMP):

$$TMP = (P_{feed} + P_{retentate})/2 - (P_{permeate}) \quad (7)$$

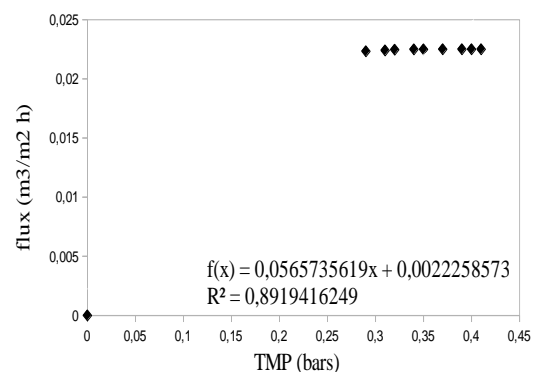


Figure 9. Effect of transmembranar pressure on the stationary natural gas flux.

The filtration flux increased linearly as a function of the transmembranar pressure until 0.37 bars. Then it is stabilized at a equilibrium constant flux

due to clogging phenomenon which restrains the flux [17]. A solid layer (cake) is built on the surface of the membrane which affects the flux of the natural gas in the membrane pores. The permeation flux is related to the transmembranar pressure according to:

$$J=Q/S=L_p.TMP \quad (8)$$

Where J is the volumetric permeation flux density, Q is the flow rate of gas permeation, S is the membrane surface and L_p is the permeability of the membrane skin. By using the results of figure 9 it is possible to deduce the permeability of the membrane skin as $L_p= 0.056 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}.\text{bars}^{-1}$.

III. Conclusion

The presence of hydrogen sulphide (H_2S) in natural gas is corrosive to the processing facilities, harmful to the public health and devastating for the environment after commercialization and consumption. The Algerian natural gas contains 0.5 % of hydrogen sulphide (H_2S). However, to be competitive this content should be reduced to an acceptable limit. The present investigation was carried out within the research framework of reducing the quantity of H_2S in natural gas by simulation of adsorption process on high density polyethylene membrane.

The kinetics calculation revealed an optimum contact time of 53 min which resulted in a maximum selectivity of 99.88 % at a feed pressure of 57.5 atm. In terms of concentration 59.07 g/l of H_2S was permeated before clogging. Longer times did not allow improving the selectivity because the pores of the polymeric membrane were saturated. In practice, this information could be very useful to set up a procedure of either changing or by passing the saturated membrane by a virgin one. As far as the temperature is concerned careful measures should be taken to avoid heat generation during the separation process as that reduces the selectivity. To avoid the clogging of the membrane it is advised to work with a transmembranar pressure below 0.37 bars and a membrane skin permeability not exceeding $0.056 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}.\text{bars}^{-1}$.

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