



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Dynamic Simulation of Hydrogen Sulfide Adsorption in a Packed Bed Column of Activated Carbon

¹S.M. Anisuzzaman, ¹D. Krishnaiah, ²C.G. Joseph, ¹S. Abang and ¹W.K. Tai

¹Chemical Engineering Programme, Faculty of Engineering,

²Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Kota Kinabalu, 88400, Sabah, Malaysia

Abstract: Petroleum has been a major energy sources to our human being in operating machine and in other usages. The high profitable petroleum is important in our daily life but before acquiring the useful products, there are also impurities such as hydrogen sulfide which is available in the crude oil that must be removed to avoid any hazard that could bring to the environment and human health. In oil refinery industry, hydrogen sulfide is commonly removed through water stripper but very little data is available on the removal of hydrogen sulfide using adsorption process. Thus, in this study, simulation modeling of adsorption of hydrogen sulfide onto activated carbon was carried out by providing respective adsorption isotherm, adsorption kinetic, mass balance and kinetic modeling. Under isothermal conditions with no pressure drop and constant velocity, the simulation had been conducted to justify the feasibility of the data provided by the industry after optimizing the size of adsorption bed that should be used. Most of the parameters should be assumed with a reasonable value in order to continue with the simulation. As a result, the actual data provided by the industry shows the feasibility of the size of adsorption bed after optimization due to the high flow rate and high hydrogen sulfide concentration.

Key words: Adsorption, isotherm, hydrogen sulfide, activated carbon, simulation

INTRODUCTION

Petroleum is a liquid that is found in a rock formation which consists of mixture of hydrocarbons in different molecular weights and also other organic compound. There are different processes in the oil and gas industry that were used to produce energy sources at different hydrocarbon products like gasoline, diesel, kerosene and other useful types of energy sources. However, crude oil refining produces by-products or impurities due to the inorganic compounds that are found in the crude oil such as hydrogen sulfide (H₂S). It also produces from hydrodesulphurization which is a common contaminant in natural gas (Reddy *et al.*, 2012).

H₂S can be found in wastewater facilities, by-product from the anaerobic digestion in the palm oil mill and food processing. H₂S with a characteristic odor of rotten egg is a raw material used to manufacture inorganic sulphides, sulphuric acid and thiols (Ouali *et al.*, 2011). Thus, the removal of H₂S from the petroleum processes is required to minimize the waste disposal (Sujo-Nava *et al.*, 2009). Besides, the main reason to remove H₂S is to minimize the corrosion formation of sulfur oxides when combusted in

the engine. The emission of H₂S to the environment causes acute poisoning and death from acute exposure to high concentration of H₂S (He *et al.*, 2011). H₂S can be in both gas and liquid form in the oil and gas industry which is known as sour gas or sour water. Sour water also consists of other inorganic compounds like ammonia which is produced from atmospheric and vacuum crude columns at the refineries (Torres *et al.*, 2013) and also from fluid catalytic cracking plants in refineries (Silva *et al.*, 2006).

This study focuses on the development of fixed bed adsorption unit to remove H₂S of sour water discharged from the oil and gas refineries. Currently, the technology implemented in the oil and gas refineries to remove hydrogen sulfide from the sour water is by using sour water stripper which is considered as the economical and unique way to treat the sour water in an industrial scale. This data used (Ho, 2012) to estimate the breakthrough time of the adsorption of H₂S onto Activated Carbon (AC), bed life span or the bed adsorptive capacity and adsorption column size. Then, the feasibility of the data provided by the oil refinery industry is determined by varying the flow rate and concentration of H₂S.

METHODOLOGY

Operating conditions of sour water: The operating conditions of sour water should be actual operating conditions which are related to the operation of a water stripper in an oil refinery industry. This limitation is set to act as a guideline to achieve the objective of this study. The operating conditions that are used are shown in Table 1.

The temperature and pressure are kept constant throughout the simulation, this is to ensure that temperature and pressure do not affect the result of the simulation which is conducted to study on the various flow rate and concentration of the H₂S by keeping one constant while varying the others. The data of flow rate and concentration of H₂S for the simulation is shown in Table 2 which is closely related with the data from the industry.

Size of adsorption bed: The size of the adsorption bed should be reasonable. The size of the adsorption bed that is needed for the simulation is the height and the internal diameter of the adsorption bed. The size of the adsorption bed is retrieved by doing optimization of the adsorption column by applying the common flow rate and concentration of H₂S to the simulation. Due to limiting the internal diameter of the adsorption bed at 1-2 m, the efficiency increases in determining the height of the adsorption bed. Besides, the main limitation of the optimization of the adsorption column is the saturation time which is to be at more than one week.

Material and momentum balance: Material and momentum balance are a function in Aspen Adsorption which is to make basic assumptions about axial dispersion in the liquid phase, to determine how to treat the pressure drop in the adsorption bed model and to specify whether the velocity is constant or varies along the column. The option of material or momentum balance in Aspen

Adsorption consist of convection only, convection with constant dispersion and convection with estimated dispersion.

The convection with constant dispersion includes the dispersion term in the material balance for the adsorption. However, the dispersion coefficient is constant for all components throughout the bed. Lastly, the convection was estimated with dispersion which includes the dispersion term in the material balance for the adsorption. With this option, the dispersion coefficient varies along the length of the bed. Aspen Adsorption estimates the values during the simulation (Aspen Tech, 2008; Anisuzzaman *et al.*, 2014) for each component using the correlation:

$$\frac{V_1 r_p}{\epsilon_i E_z} = \frac{0.2}{\epsilon_i} + \frac{0.011}{\epsilon_i} \left(\frac{R_e}{\epsilon_i} \right)_{0.48} \tag{1}$$

Where:

- E_z = Axial dispersion coefficient
- V₁ = Liquid velocity
- ε_i = Interparticle voidage (bed voidage)
- r_p = Particle radius
- R_e = Reynolds number

Convection with estimated dispersion was selected for the simulation of adsorption of H₂S onto AC. This is due to the internal diameter of the adsorption bed is large, thus dispersion should not be omitted. However, convection with constant dispersion does not provide enough information for the simulation compared to convection with estimated dispersion which is required additional information like adsorbent particle radius. Thus, the values needed to be inserted into the simulation are inter-particle voidage (bed voidage), intra-particle (particle porosity), adsorbent particle radius and solid density. The bed voidage could be obtained from the value of macropore which is in the range of 0.2-0.5 and value of micropore in the range of 0.15- 0.5 is used as the value for particle porosity in the simulation model. The adsorbent particle radius is obtained by assuming the AC used in the adsorption column is a granular AC which the particle size is in the range of 0.5-4 mm. The density of the AC is 0.427 g mL⁻¹ (Xiao *et al.*, 2008). Besides that, assuming there is no pressure drop assumption and the velocity assumption is considered to be constant. For energy balance, isothermal condition is assumed.

Kinetic model: The rate of physical adsorption is generally high on the surface of the porous catalyst or adsorbent when the overall rate of adsorption is always controlled by mass or heat transfer resistance, rather than by the intrinsic sorption kinetics (Ruthven, 1984). When

Table 1: Parameter needed for the simulation of H₂S (Lee *et al.*, 2002)

Parameters	Values
Temperature (°C)	30
Pressure (atm)	1
Flow rate (m ³ year ⁻¹)	80,700
H ₂ S (mg L ⁻¹)	2500

Table 2: Varying of flow rate and concentration of H₂S

Flow rate (m ³ year ⁻¹)	Conc. (mg L ⁻¹)	Conc. (mol L ⁻¹)
80.7	2.5	7.34×10 ⁻⁵
807	25	7.34×10 ⁻⁴
8070	250	7.34×10 ⁻³
80700	2500	7.34×10 ⁻²

the adsorbate is adsorbed from the bulk liquid phase onto the an active surface site of the adsorbents, it typically experiences the mass transfer resistances between the bulk liquid and the external adsorbents surface and the resistance exerted by the adsorbents pore structure. The resistances are typically lumped into a single and overall mass transfer coefficient. For kinetic model assumption, the options are linear lumped resistance, micro and macropore and quadratic lumped resistance. Micro and macropore is suitable for bi-disperse adsorbents such as zeolites, thus micro and macropore is not selected. For the adsorption of H₂S onto AC, linear lumped resistance is sufficient when the mass transfer driving force for H₂S is expressed as a linear function of liquid phase concentration:

$$\rho_s \frac{\partial w_i}{\partial t} = MTC_{li} (c_i - c'_i) \quad (2)$$

Where:

- ρ_s = Adsorbent bulk density (kg m⁻³)
- w_i = Loading of component I (kmol kg⁻¹)
- t = Time (sec)
- MTV_{li} = Liquid film mass transfer coefficient (L sec⁻¹)
- c_i = Bulk liquid phase concentration of component I (kmol m⁻³)
- c'_i = Liquid phase composition at equilibrium with the actual loading (kmol m⁻³)

The constant mass transfer coefficient is obtained from Table 3 with the effective diffusivity (m²sec⁻¹) of H₂S adsorption on AC.

Isotherm model: The driving force behind all adsorptive liquid separation processes is the departure from adsorption equilibrium, so adsorption isotherms are important in adsorber design. It is used for the analysis of adsorption process as it describes how the adsorbate interacts with adsorbent once it reaches the equilibrium. Among the isotherms option in Aspen Adsorption, Langmuir isotherm is selected. It is based on the four hypotheses which are; the surface of the adsorbent is uniform, adsorption sites are equal, adsorbed molecules do not interact, all adsorption occurs through the same mechanism and at the maximum adsorption, only a monolayer is formed. The molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. For the adsorption of liquid onto the solids, Langmuir isotherm can be expressed as:

Table 3: Effective diffusivity (m² sec⁻¹) of H₂S adsorption on AC (Xiao *et al.*, 2008)

Concentration (ppm)	Effective diffusivity (m ² sec ⁻¹)
200	1.59×10 ⁻⁶
400	1.68×10 ⁻⁶
600	1.75×10 ⁻⁶
1000	2.01×10 ⁻⁶

Table 4: Langmuir isotherm parameters obtained by using linear method under dry condition (Xiao *et al.*, 2008)

Parameters	Values
q_m	2.7
K_L	0.014

$$q = \frac{q_m K_L C_p}{1 + K_L C_p} \quad (3)$$

Where:

- q = The substance amount of adsorbate adsorbed per gram of the adsorbent
- q_m = Maximal substance amount if adsorbate per gram of the adsorbent
- K_L = Adsorption constant
- C_p = Concentration of adsorbate in liquid

The Langmuir isotherm parameters are preterited in Table 4.

RESULT AND DISCUSSION

Optimization of adsorption bed size: Considering at the feed to the adsorption column, the required parameters for optimization are the flow rate, concentration, temperature and pressure. The temperature for the operation is at 30°C and the pressure is at atmospheric condition is 1 atm. The flow rate, as stated in Table 2, shows the unit is at m³ year⁻¹ which is similar as in the simulation. However, the concentration of the H₂S was recalculated to obtain a unit similar to the simulation model.

The height and diameter of adsorbent layer were assumed. The diameter of the adsorbent layer was set at 2 m while the height of the adsorbent layer varies. By try and error, the height which has a saturation time of more than one week was found to be 10 m. Figure 1 shows the breakthrough curve of H₂S at optimum parameters. Other than that, the flow rate and concentration of H₂S which had been assumed as optimum parameter were 807 m³ year⁻¹ and 7.34 7.34×10⁻¹ mol L⁻¹.

The saturation time at the optimum condition was estimated at 850000 sec which is about 9.8 days or approximately 10 days if the plant operates for 24 h. Thus, this shows that the parameters used to optimize the optimum adsorption bed size were acceptable as it is more than one week. Thus, the flow rate of 807 m³ year⁻¹ and concentration of 0.00734 mol L⁻¹ were used for the

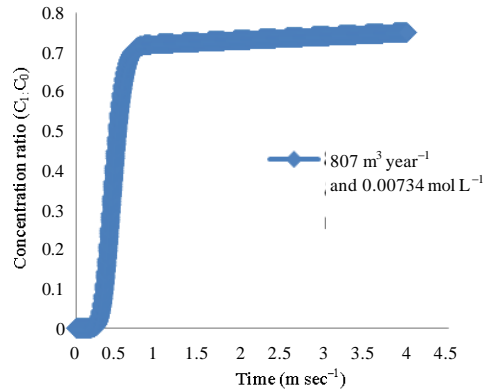


Fig. 1: Breakthrough of H₂S at optimum parameters

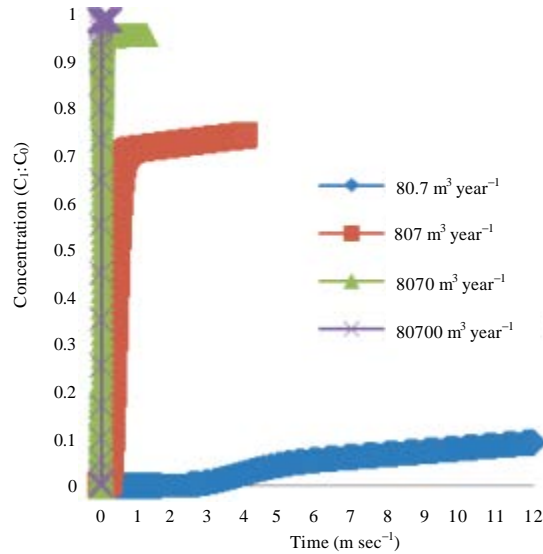


Fig. 2: Breakthrough curve of H₂S at various flow rates

simulation. The simulation can be conducted by keeping one of the properties constant while varying the other.

For the inter-particle voidage which is the bed voidage had been assumed as the macropore volume and the intra-particle voidage which is the particle porosity, assuming the macropore volume to be 0.4 and micropore volume to be 0.35 in the simulation. For the adsorbent particle radius, granular activated carbon had been used so the range of the particle size is in 0.5-4 mm. The particle size of the AC is 1 mm. The solid density is also the density of the AC used in the adsorption column. The apparent density of the AC is 0.427 g mL⁻¹.

Values for the parameters of the isotherm can be directly retrieved from Table 4 without any changes of

units. Constant mass transfer coefficient had been derived from the effective diffusivity (m² sec⁻¹) from Table 3. Table 5 shows the mass transfer coefficient of H₂S adsorption on AC.

Comparison between the flow rates of H₂S: By keeping the parameters constant, varying the flow rates of H₂S, show significant differences in results between the various flow rates. Figure 2 shows the breakthrough curve of hydrogen sulfide at various flow rates. The flow rates from the Table 5 are used in the simulation while the concentration is kept constant at 0.00734 mol L⁻¹. The large different in flow rates shows that the saturation time is achieved at a slower rate at low flow rate while, the high

Table 5: Mass transfer coefficient of H₂S adsorption on AC

Parameters	Concentration (ppm)			
	200	400	600	1000
Effective diffusivity (m ² sec ⁻¹)	1.59×10 ⁻⁶	1.68×10 ⁻⁶	1.75×10 ⁻⁶	2.01×10 ⁻⁶
Time (L sec ⁻¹)	5.06×10 ⁻⁷	5.34×10 ⁻⁷	5.57×10 ⁻⁷	6.40×10 ⁻⁷

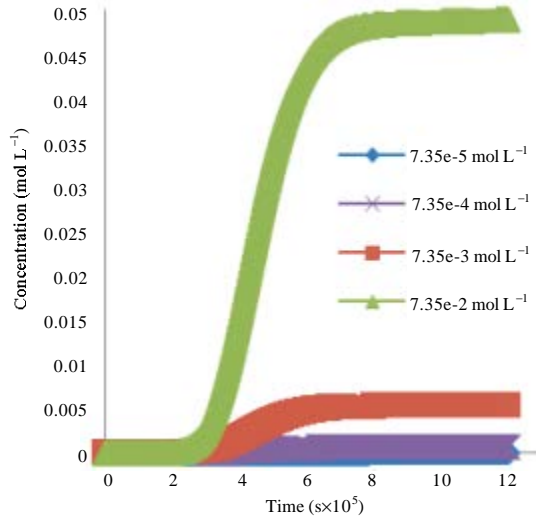


Fig. 3: Effect of concentration of H₂S against time

flow rate is achieved saturation time at a faster speed. This happens because at low flow rate, the adsorption of H₂S onto the active site of the adsorbent is less which will not block the active sites rapidly. However, at high flow rates of the H₂S at a higher speed at which the adsorption of H₂S to the active site of the AC rapidly increases, results in blockage of active sites of AC at a faster rate.

The estimated saturation time from the graph for the different flow rates 807, 8070 and 80700 m³ year⁻¹ are 850000, 80000 and 8000 sec, respectively. It is also equivalent to 9.84, 0.93 and 0.09 days. The flow rate of 80.7 m³ year⁻¹ is required very long time to saturate. This is because the flow does not provide enough H₂S for adsorption. Other than that, Fig. 2 shows that the lower flow rate takes a longer time to reach the concentration ratio of 1 than the higher flow rates. This shows that the data provided by the oil refinery industry is not feasible at high flow rate; this is because the saturation time is too short which the adsorption bed had to be replaced more frequent. Thus, this could increase the maintenance cost for which more labour is needed to change the adsorption bed. In order to solve the problem, an adjustment of the flow rate to optimum flow rate is to be conducted. Furthermore, the micro-macropore resistance assumption did not applied in the simulation of the higher flow rate. Thus, the saturation time for the higher flow rate achieved faster.

Comparison between the concentrations of H₂S: To retrieve the result of breakthrough curve by varying concentration of H₂S, the flow rate of the H₂S was to be kept constant. At a constant flow rate, the saturation time did not affect too much even when the concentration is varied. This was because the mass transfer in the adsorption column is constant when the rate of adsorption of H₂S onto the AC was the same. However, at higher concentration, the mass transfer coefficient was changed, thus the saturation time slightly deviated from the other saturation time at different concentration. Figure 3 shows the effect of concentration of H₂S against time. It shows that the feed is achieved an equilibrium curve at low concentration while the others achieved equilibrium curve at high concentrations. Eventually, all the feed was reached the equilibrium at the similar time but at different level of concentration.

Figure 4 shows the breakthrough curve of H₂S at various concentrations. It shows that at constant flow rate and mass transfer coefficient, the breakthrough curve produce similar ratio. The graphs were overlapped onto each other except for the concentration when the mass transfer coefficient changed. The increasing of mass transfer coefficient due to the increase of concentration reduced the level of equilibrium, while maintaining the similar saturation time with the other different concentrations.

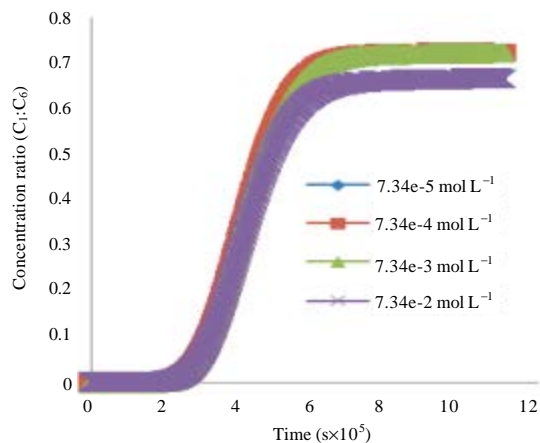


Fig. 4: Breakthrough curve of H₂S at various concentrations

CONCLUSION

The results from the simulation show that the simulation of the adsorption of H₂S onto AC is not feasible with oil refinery industry parameters. This is because the oil refinery produces high concentration of H₂S content sour water with high flow rate. This could be easily saturated by using an optimum adsorption column with the height of adsorbent layer of 10 m and internal diameter of adsorbent layer of 2 m. The result shows that the estimated saturation time for the different flow rates 807, 8070 and 80700 m³ year⁻¹ are 850000, 80000 and 8000 sec, respectively. It is also equivalent to 9.84, 0.93 and 0.09 days. The flow rate of 80.7 m³ year⁻¹ took a long time to saturate for the same concentration.

REFERENCES

Anisuzzaman, S.M., A. Bono, D. Krishnaiah and Y.Z. Tan, 2014. A study on dynamic simulation of phenol adsorption in activated carbon packed bed column. *J. King Saud Univ.-Eng. Sci.* 10.1016/j.jksues.2014.01.001

Aspen Tech, 2008. Aspen one V7.1 deployment guide. ftp://chemeng-old.chee.queensu.ca/aspen%20stuff/documentation%20disk/AspenOneV7_0-Dply.pdf.

He, R., F.F. Xia, J. Wang, C.L. Pan and C.R. Fang, 2011. Characterization of adsorption removal of hydrogen sulfide by waste biocover soil, an alternative landfill cover. *J. Hazardous Mater.*, 186: 773-778.

Ho, N., 2012. Modeling hydrogen sulfide adsorption by activated carbon made from anaerobic digestion by-product. Master's Thesis, University of Toronto, Canada.

Lee, D., J.M. Lee, S.Y. Lee and I.B. Lee, 2002. Dynamic simulation of the sour water stripping process and modified structure for effective pressure control. *Chem. Eng. Res. Design*, 80: 167-177.

Ouali, S., S. Chader, M. Belhamel and M. Benziada, 2011. The exploitation of hydrogen sulfide for hydrogen production in geothermal areas. *Int. J. Hydrogen Energy*, 36: 4103-4109.

Reddy, E.L., V.M. Biju and C. Subrahmanyam, 2012. Production of hydrogen from hydrogen sulfide assisted by dielectric barrier discharge. *Int. J. Hydrogen Energy*, 37: 2204-2209.

Ruthven, D.M., 1984. Principles of Adsorption and Adsorption Processes. John Wiley and Sons, New York, ISBN: 9780471866060, Pages: 433.

Silva, R.S.E., M.D.F.B. de Carvalho and R.E. Santelli, 2006. Separation and determination of metalocyanide complexes of Fe (II), Ni (II) and Co (III) by ion-interaction chromatography with membrane suppressed conductivity detection applied to analysis of oil refinery streams (sour water). *J. Chromatography A*, 1127: 200-206.

Sujo-Nava, D., L.A. Scodari, C.S. Slater, K. Dahm and M.J. Savelski, 2009. Retrofit of sour water networks in oil refineries: A case study. *Chem. Eng. Process.: Process Intensification*, 48: 892-901.

Torres, C.M., M. Gadalla, J.M. Mateo-Sanz and L. Jimenez, 2013. An automated environmental and economic evaluation methodology for the optimization of a sour water stripping plant. *J. Cleaner Product.*, 44: 56-68.

Xiao, Y., S. Wang, D. Wu and Q. Yuan, 2008. Experimental and simulation study of hydrogen sulfide adsorption on impregnated activated carbon under anaerobic conditions. *J. Hazardous Mater.*, 153: 1193-1200.