

MODELING OF H₂S ADSORPTION WITH HYDROGEL BIOCHAR

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Abstract—The purpose of this study is to model the adsorption of sour gas on hydrogel biochar bio adsorbent. Conventional activated carbon is expensive and has environmental concerns since it is not bio-degradable which leads to the attention in finding a cheaper, eco-friendly material from readily available renewable sources and hydrogel is seen as a viable alternative. Adsorption tests have been carried out in a fixed-bed column, at different flowrate of 200 L/h, 100 L/h and 50 L/h and at varying bed heights in order to investigate the kinetic parameters. It was established that the adsorbent has a good H₂S adsorption capacity, owing to its surface area and composition. H₂S adsorption rate increases with lower inlet flowrate while higher bed height increases the adsorption capacity. The experimental data was fitted with pseudo-first order and pseudo-second order and it is found the first order best describes the adsorption process at sufficiently high inlet flowrate.

Keywords— *Adsorption, adsorption column, hydrogel biochar, Matlab, modeling.*

I. INTRODUCTION

Hydrogen sulphide is considered as a hazardous substance for its toxic nature that causes various health issues that can be lethal. Emission of this gas to the environment also leads to formation acid rain or fog. To control the emission of this hazardous gas to the atmosphere, there are various approaches and technologies utilized in industries with adsorption being the most extensive process in gas treatment. For these past decades, there have been rapid development and continuous research in effort to improve adsorption of sour gas with focus on producing materials with better performance as adsorbent. Activated carbon is a widely used adsorbent for separation of sour gas for its flexibility and efficiency. However, conventional activated carbon is expensive and has environmental concerns since it is not bio-degradable. This leads to the attention in finding a cheaper, eco-friendly material from readily available renewable sources. Superabsorbent hydrogel is seen as an excellent alternative to activated carbon for use in adsorption processes because of the properties which fulfils the requirement for a good adsorbent. There have been developments for producing superabsorbent hydrogels with features such as high gel strength and larger surface area to improve its capability as an adsorbent. In order to maximize the efficiency of adsorption of sour gas by hydrogel biomass composite adsorbent, there is an urgent need for kinetics study to investigate the parameters affecting the phenomena for optimization purposes. This can be done by the study of mathematical models which describes the complex adsorption process. Adsorption process modelling reveals the performance of adsorbent and the influence of different parameters for the adsorption process.

II. METHODOLOGY

A. Biochar preparation from sugarcane

Biochar is produced via pyrolysis process. Pyrolysis is thermal degradation of an organic material at relatively low temperature with no oxygen. Biochar for this study is derived from sugarcane bagasse produced with microwave pyrolysis. The sugarcane bagasse is left to dry to remove moisture content before filling in the reactor. The reactor then placed inside the microwave with nitrogen as inert gas being pumped to remove inside oxygen for around thirty minutes. Next, pyrolysis occurs inside the microwave at a condition of 1000°C which takes another thirty minutes. The resulting biochar is left to cool for thirty minutes. The whole pyrolysis process is only around one hour and a half. The biochar then washed with 0.1mol/L HCL for 6 hours for demineralization followed by washing with deionized water to neutralize back the biochar. Lastly, biochar was dried in an oven at 40°C for a day.

B. Preparation of hydrogel-biochar

Hydrogel is obtained through polymerization and cross linking of the biochar. To explain the process briefly, 1.0 g of AAm dissolved in 1 mL DI water to form a solution which was added 0.6 g biochar and 0.001 g of MBA. Polymerization initiated with addition of 0.2 mL of APS aqueous solution. Hydrogel precursor placed instantly to PVC straw and left for a day to ensure completion of process. The resulting hydrogel biochar composite then cut to suitable sizes and washed with DI water to remove monomers. Next, hydrogel biochar dried in air and left in a vacuum oven at 40°C for a day. Finally, samples placed in desiccator for further use.

C. Adsorption test

Adsorption column is the equipment to study the adsorption process of hydrogen sulphide. The equipment consists of two columns, each with three layers of adsorption tray. The column is made from stainless steel making it suitable for use with corrosive gas. Glass wool applied between trays to avoid passing of particles and clogging of gas. The equipment is activated using the main switch for start-up. After starting the temperature controller will show the set temperature and mass flow controller should display a value of zero. The gas absorber has two inlets which come with a flow controller.

The experimental parameters for study of adsorption performance include effect of gas flowrate and effect of adsorbent bed height. For study of flowrate, the experiment is run with three different flowrate which is 200 L/h, 100 L/h and 60 L/h at constant temperature. The variables are set using the control instrument which are the temperature controller and flowmeter.. Further study is done by running the adsorption process with different bed height of 1.5 inch, 3 inch and 6 inch of hydrogel adsorbent.

D. MATLAB

MATLAB software to simulate experimental data. The kinetic models are compared and validated by analysing the results. Cftool is a feature of MATLAB to aid in analysis and fitting of data to obtain linear form of equations for respective models. The suitability for each mathematical model is determined by using the R² values and coefficients to evaluate accuracy of fitted data.

E. Kinetic studies

The research of adsorption kinetics describes the H₂S uptake rate which equation shows the relation of adsorbent uptake at the solid-gas interface with time. In this study, two kinetic models which are the pseudo first order equation and pseudo second order equation were applied to find out the adsorption mechanism.

Lagergren's pseudo-first-order kinetic is one of the earliest model pertaining to adsorption rate based on the adsorption capacity. The process of toxic gas removal from liquid or gaseous phase by adsorbent is expressed in the form:

$$\log(q_e - q_t) = \log q_e - K_p1t \quad (1)$$

where q_t is the amount adsorbed (mg/g) at various time t , q_e is the equilibrium adsorption capacity (mg/g), K_p1 the pseudo-first-order rate constant for the adsorption process. The pseudo first order considers the rate of occupation of adsorption sites is directly proportional to the number of unoccupied sites.

Pseudo-second-order kinetic model proposed by Ho,1999, is an extension to the pseudo-first order for adsorption process which occurs between one molecule of adsorbate and two adsorption sites. The pseudo-second-order kinetic equation is expressed in the form:

$$t/q_t = (1/q_e)t + (1/K_{p2}q_e^2) \quad (2)$$

where q_t is the amount adsorbed (mg/g) at various time t , q_e the equilibrium adsorption capacity (mg/g), K_{p2} the pseudo-second-order rate constant. The plot of data gives a linear relationship and the obtained value of R^2 and q_e is compared to evaluate the suitability of model.

III. RESULTS AND DISCUSSION

A. Effect of inlet gas flowrate

The effect of different inlet flowrate of Hydrogen Sulphide gas has been studied by evaluating the adsorption performance on various flowrate of 60 L/hour, 100 L/hour and 200 L/hour. The bed height of adsorbent inside column kept at 6 inch adsorbent bed height with inlet gas concentration of 25. Temperature was kept constant at 27 °C throughout the experiment.

In order to determine the H₂S efficiency by the composite hydrogels, the two kinetic models pseudo-first-order and pseudo-second-order were applied to fit the adsorption process. The fitted data for pseudo –first order models are shown in Figure 1 to Figure 3.

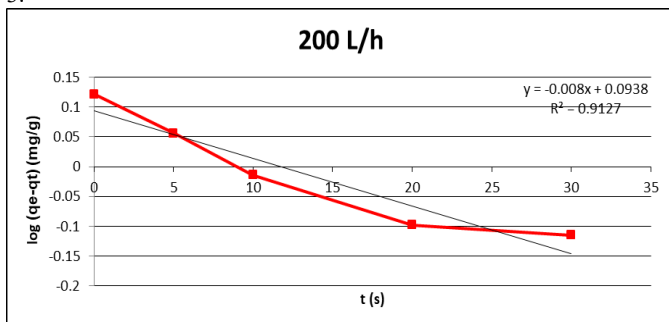


Fig. 1: Pseudo-First-Order Model for inlet flowrate of 200 L/h

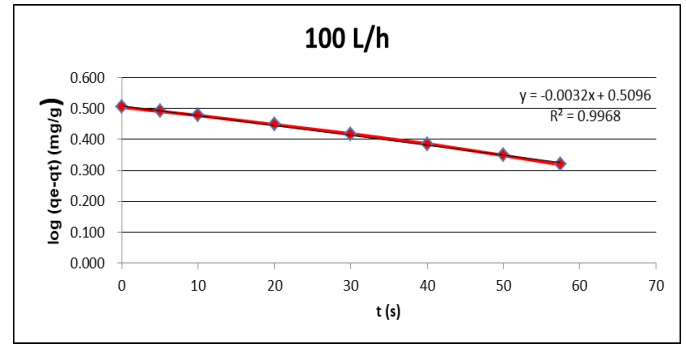


Fig. 2: Pseudo-First-Order Model for inlet flowrate of 100 L/h

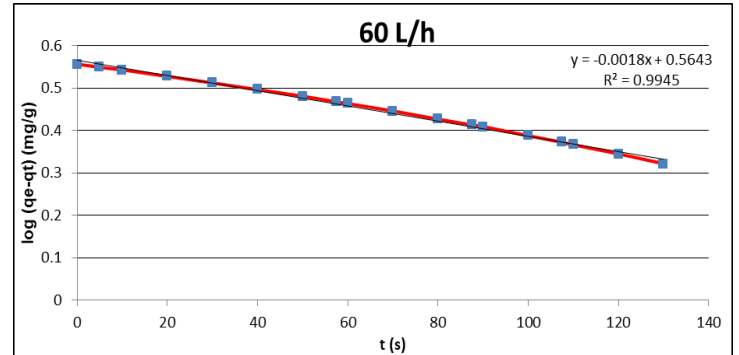


Fig. 3: Pseudo-First-Order Model for inlet flowrate of 60 L/h

Table 1 represents the obtained correlation coefficients obtained from the linearized equation from Fig.1 to Fig.3.

Table 1: Pseudo-first-order model parameters

Flowrate (L/h)	q_e (cal) (mg/g)	K_{p1} (1/s)	R^2
200	1.24	0.008	0.9127
100	3.23	0.0032	0.9968
60	3.67	0.0018	0.9945

The values of R^2 obtained shows that pseudo-first order model fits very well with the adsorption process. The value of adsorption capacity, q_e from the equation is close with the experimental value which are 1.3 mg/g for 200 L/h, 3.2 for 100 L/h and 3.6 for 60 L/h. The close values of calculated and experimental adsorption capacity imply that the adsorption process follows the pseudo-first order relation when the flowrate of H₂S is sufficiently high. The property a pseudo-first-order process is that the rate of occupation of adsorption sites of hydrogel adsorbent is directly proportional to the number of unoccupied sites, as presented from the straight line of plot (J.Thilagan, 2013).

As for pseudo-second-order, the plotted data is shown in Figure 4 to Figure 6.

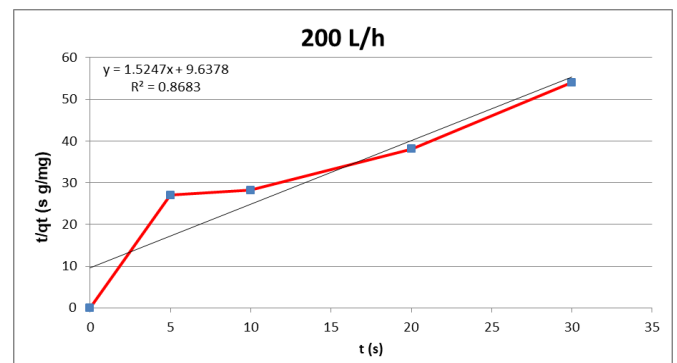


Fig. 4: Pseudo-Second-Order Model for inlet flowrate of 200 L/h

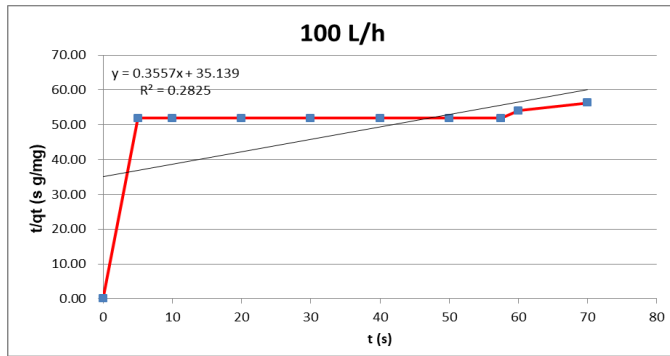


Fig. 5: Pseudo-Second-Order Model for inlet flowrate of 100 L/h

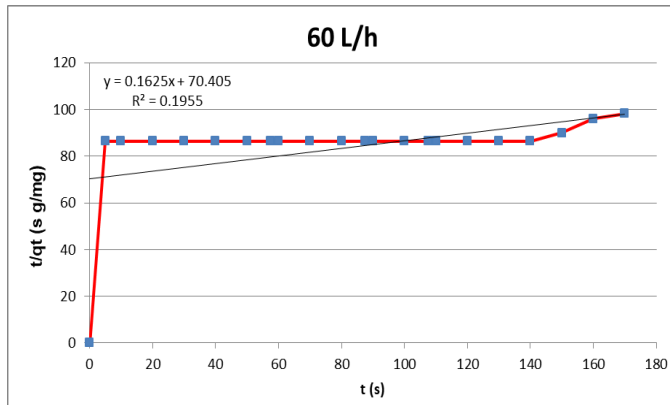


Fig. 6: Pseudo-Second-Order Model for inlet flowrate of 60 L/h

Table 2 represents data obtained from Fig. 13 to Fig. 15.

Table 2: Pseudo-second-order model parameters

Flowrate (L/h)	qe (cal) (mg/g)	Kp ₂ (g/mgs)	R ²
200	0.66	0.008	0.8683
100	2.81	0.0032	0.2825
60	6.15	0.0018	0.1955

The results show decreasing R2 value with decreasing flowrate. The obtained value of adsorption capacity, qe deviates further with varying flowrate and that does not compare well with the actual adsorption capacity from experiment. Thus, this model is unsuitable for use in this adsorption process and further strengthen the conclusion that this adsorption process is governed by pseudo-first-order kinetic. This result is contrary to expectation since previous studies found that the pseudo-second-order is best in describing the kinetics for gas-solid adsorption of H₂S. This may be due to the high inlet flowrate of H₂S tested for this experiment. There is a large quantity of adsorbate that flows into the system compared to the physical amount adsorbent so the reaction can be treated as a first order reaction by neglecting the lower amount reactant.

Both kinetic models show an increasing adsorption capacity with decreasing flowrate. The pseudo-first-order equation gives qe value that increases from 1.24 mg/g to 3.67 mg/g and calculated qe of 0.66 mg/g to 6.15 mg/g for pseudo-second order when the flowrate decreases from 200 L/h to 60 L/h. The better adsorption capacity at lower flowrate is due to the longer contact time for gas stream to interact with adsorbent thus improving removal of H₂S. At high flowrate, the process is too fast to reach saturation.

B. Effect of bed height

The effect of different inlet flowrate of Hydrogen Sulphide gas has been studied by evaluating the adsorption performance on various flowrate of 60 L/hour, 100 L/hour and 200 L/hour. The bed height of adsorbent inside column kept at 6 inch adsorbent bed height with inlet gas concentration of 25. Temperature was kept

constant at 27 °C throughout the experiment. The fitted data for pseudo –first order models are shown in Figure 7 to Figure 9.

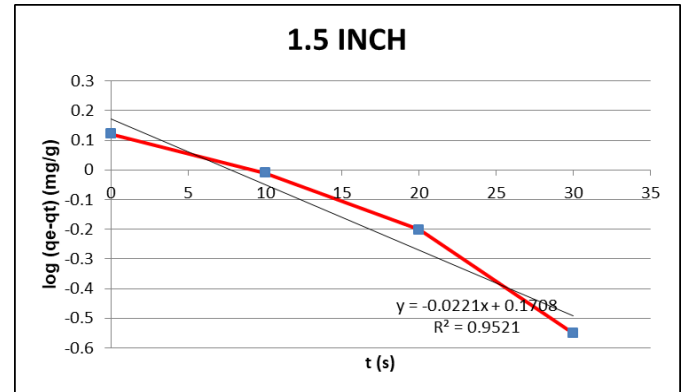


Fig. 7: Pseudo-First-Order Model for 1.5 inch of hydrogel

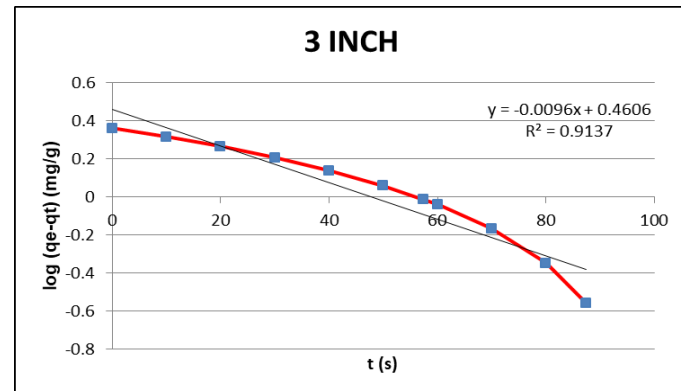


Fig. 8: Pseudo-First-Order Model for 3 inch of hydrogel

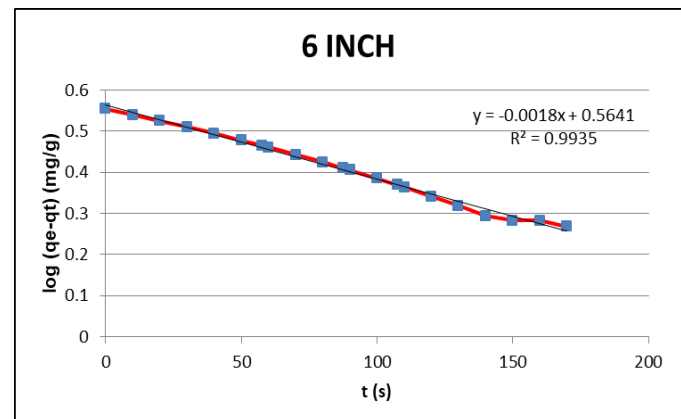


Fig. 9: Pseudo-First-Order Model for 6 inch of hydrogel.

Parameters of the fitted data is tabulated in Table 3.

Table 3: Pseudo-first-order model parameters

Bed height (inch)	qe (cal) (mg/g)	Kp ₂ (g/mg s)	R ²
1.5	1.48	2.67	0.9521
3	2.89	0.26	0.9137
6	3.67	0.13	0.9935

The adsorption process still follows pseudo-first-order kinetics even when the bed height varies from 1.5 inch 6 inch signifying the process is still fast enough at the supplied gas flowrate that physisorption becomes dominant. The pseudo-first-order model fits the adsorption process very well as seen from the value of R2 that is close to 1 for all bed height so the process can be assumed as a first order system.

Figure 10 to 12 shows the plot for pseudo-second-order model.

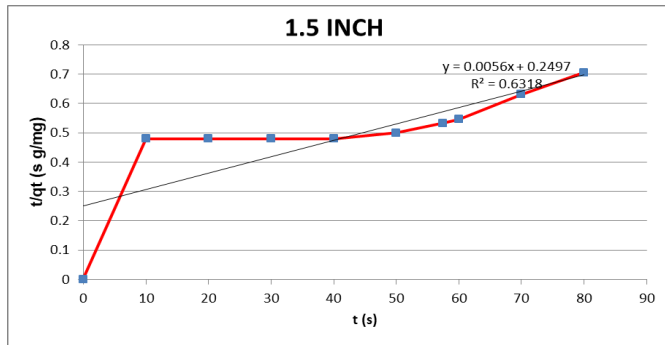


Fig. 9: Pseudo-First-Order Model for 1.5 inch of hydrogel.

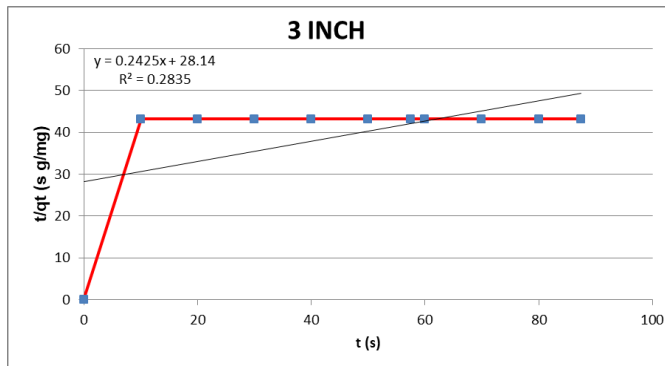


Fig. 10: Pseudo-Second-Order Model for 3 inch of hydrogel.

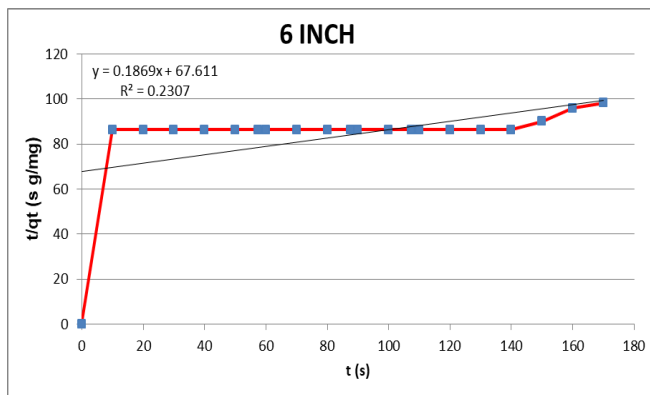


Fig. 11: Pseudo-Second-Order Model for 6 inch of hydrogel.

Parameters of the fitted data is tabulated in Table 4.

Table 4 : Pseudo-second-order model parameters

Bed height (inch)	qe (cal) (mg/g)	Kp ₂ (g/mg s)	R ²
1.5	178.57	0.00013	0.6318
3	4.12	0.002	0.2835
6	5.35	0.13	0.2307

The fitted data gives a low value of R² for the three bed height meaning that the model is inapplicable for kinetic studies of adsorption process at this specific parameter. The adsorption capacity from the equation is unreliable for very fast process as it greatly differs from the experimental value especially at a smaller scale as seen from the lowest bed height. It is also observed that the value of R² decrease for process with longer exposure time indicating that the pseudo-second-order equation is not efficient for use in process that take a long time.

From the obtained result in Table 3, increasing the bed height will cause the adsorption capacity to increase. This phenomenon is due to the lesser amount of hydrogel with shorter bed length meaning less available active site. Longer bed length naturally gives better adsorption capacity due to more presence of active site thus more effective removal. Lower adsorption capacity at shorter adsorbant bed also gives a lower contact time thus less removal of

H₂S for a set period. A study by Azil, et al., 2018 also shows a similar result of increasing adsorption capacity with bed height as the q_e increase from 0.05 to 1.44 when adsorbent height increased from 1.5 inch to 6 inch.

IV. CONCLUSION

Based on adsorption study of H₂S adsorption on various parameter, hydrogel is shown to be a capable and feasible alternative to current industrial adsorbents such as activated carbon which is expensive and has adverse effect to the environment.

Kinetic studies were done for optimization purposes and it is found that pseudo-first-order model best describes the process where the flowrate is sufficiently high and for fast process. The values of adsorption capacity obtained from pseudo-first-order for the tested conditions are similar to experimental value compared to pseudo-second-order so it can be assumed that the process follows first order kinetics which assume physisorption is the dominant mode of adsorption.

Both kinetic models show an increasing adsorption capacity with decreasing flowrate. The pseudo-first-order equation gives q_e value that increases from 1.24 mg/g to 3.67 mg/g and calculated q_e of 0.66 mg/g to 6.15 mg/g for pseudo-second order when the flowrate decreases from 200 L/h to 60 L/h. The better adsorption capacity at lower flowrate is due to the longer contact time for gas stream to interact with adsorbent thus improving removal of H₂S.

As for effect of bed height, the adsorption capacity is seen to increase with longer bed length for both experimental and calculated from model equation. More H₂S can be absorbed at longer bed length simply due to more presence of active site. This phenomenon is due to the lesser amount of hydrogel with shorter bed length meaning less available active site.

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References

- Ahmed, E. M. (2015) 'Hydrogel: Preparation, characterization, and applications: A review', *Journal of advanced research*. Cairo University, 6(2), pp. 105–21. doi: 10.1016/j.jare.2013.07.006.
- Alias, A. B. et al. (2018) 'Modelling of Adsorption Kinetic and Equilibrium Isotherms of Hydrogen Sulfide onto Hydrogel Biochar Adsorbent', 7, pp. 369–375.
- Baccar, R. (2013) 'Removal of water pollutants by adsorption on activated carbon prepared from olive- waste cakes and by biological treatment using ligninolytic fungi', (July), p. 274.
- Bamdad, H., Hawboldt, K. and MacQuarrie, S. (2018) 'A review on common adsorbents for acid gases removal: Focus on biochar', *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 81(May), pp. 1705–1720. doi: 10.1016/j.rser.2017.05.261.
- Bolis, V. (2013) *Calorimetry and Thermal Methods in Catalysis*. doi: 10.1007/978-3-642-11954-5.
- Cherif, H. (2018) 'Study and modeling of separation methods H₂S from methane, selection of a method favoring H₂S valorization Hamadi Cherif To cite this version : HAL Id : tel-01764942 THÈSE DE DOCTORAT de l'Université de recherche Paris Sciences et Lettres Préparée à MI'.
- Chung Lau, L. (2017) 'Adsorption Isotherm, Kinetic, Thermodynamic and Breakthrough Curve Models of H₂S Removal Using CeO₂/NaOH/PSAC', *International Journal of Petrochemical Science & Engineering*, 1(2). doi: 10.15406/ipcse.2016.01.00009.
- Dąbrowski, A. (2001) 'Adsorption - From theory to practice', *Advances in Colloid and Interface Science*, 93(1–3), pp. 135–224. doi: 10.1016/S0001-8686(00)00082-8.

- Fahanwi, A. N. (2014) 'Synthesis and Characterization of Superabsorbent Chitosan-Starch Hydrogel and its Application for Removal of Direct Red 80 Dye', (January).
- Guo, Y. and Du, E. (2012) 'The Effects of Thermal Regeneration Conditions and Inorganic Compounds on the Characteristics of Activated Carbon Used in Power Plant', *Energy Procedia*, 17, pp. 444–449. doi: 10.1016/j.egypro.2012.02.118.
- Habeeb, O.A., Ramesh, K., Gomaa Ali, A.M., Yunsu, R.M., Thanusha, T. K. and Olarere, O. A. (2016) 'Modeling and Optimization for H₂S Adsorption from Wastewater Using Coconut Shell Based Activated Carbon', *Australian Journal of Basic and Applied Sciences*, 10(17), pp. 136–147.
- Hervy, M. *et al.* (2018) 'H₂S removal from syngas using wastes pyrolysis chars', *Chemical Engineering Journal*, 334, pp. 2179–2189. doi: 10.1016/j.cej.2017.11.162.
- Ho, N. and Kirk, D. (2012) 'Modeling Hydrogen Sulfide Adsorption by Activated Carbon made from Anaerobic Digestion By-Product', *Department of Chemical Engineering and Applied Chemistry*, M.Sc.
- important to understand (1996) 'The Langmuir Adsorption Isotherm', *Help To Understand Langmuir Isotherm*, 49(3–4), pp. 247–259. doi: 10.1080/00207239608711028.
- Investigation, E. (1992) 'Basic Principles of Adsorption', pp. 36–47.
- Iruretagoyena Ferrer, D. (2016) *Supported Layered Double Hydroxides as CO₂ Adsorbents for Sorption-enhanced H₂ Production*. doi: 10.1007/978-3-319-41276-4.
- Khan, M. and Lo, I. M. C. (2016) 'A holistic review of hydrogel applications in the adsorptive removal of aqueous pollutants: Recent progress, challenges, and perspectives', *Water Research*. Elsevier Ltd, 106, pp. 259–271. doi: 10.1016/j.watres.2016.10.008.
- Lennard, J. E. (1932) 'Chapter 2 Physical Adsorption', pp. 13–71.
- M. Dharmendirakumar, G. Vijayakumar, R. T. *et al.* (2015) 'Adsorption , Kinetic , Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from ...', *Journal of Materials and Environmental Science*, 3(June), pp. 157–170.
- Meri, N. H. *et al.* (2018) 'Comparison of H₂S adsorption by two hydrogel composite (HBC) derived by Empty Fruit Bunch (EFB) biochar and Coal Fly Ash (CFA)', *IOP Conference Series: Materials Science and Engineering*, 334(1). doi: 10.1088/1757-899X/334/1/012038.
- O *et al.* (2018) 'Kinetic, Isotherm and Equilibrium Study of Adsorption Capacity of Hydrogen Sulfide-Wastewater System Using Modified Eggshells', *IJUM Engineering Journal*, 18(1), pp. 13–25. doi: 10.31436/ijumej.v18i1.689.
- Of, O. (2017) 'ISOTHERMAL MODELLING BASED EXPERIMENTAL STUDY OF DISSOLVED HYDROGEN SULFIDE ADSORPTION FROM WASTE WATER (Model Isoterma Berdasarkan Kajian Penjerapan Hidrogen Sulfida Terlarut daripada Air Sisa', 21(2), pp. 334–345.
- Okay, O. (2010) 'Hydrogel Sensors and Actuators', 6, pp. 1–15. doi: 10.1007/978-3-540-75645-3.
- Popp, J. A. *et al.* (2007) 'A Critical Review of the Literature on Hydrogen Sulfide Toxicity', *CRC Critical Reviews in Toxicology*, 13(1), pp. 25–97. doi: 10.3109/10408448409029321.
- Possa, R. D. *et al.* (2018) 'Dynamic Adsorption of H₂S in a Fixed Bed of Sewage Sludge Pyrolysis Char', *Brazilian Journal of Petroleum and Gas*, 12(2), pp. 77–90. doi: 10.5419/bjg2018-0008.
- Sethupathi, S. *et al.* (2017) 'Biochars as potential adsorbers of CH₄, CO₂ and H₂S', *Sustainability (Switzerland)*, 9(1), pp. 1–10. doi: 10.3390/su9010121.
- Shafeeyan, M. S., Wan Daud, W. M. A. and Shamiri, A. (2014) 'A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption', *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 92(5), pp. 961–988. doi: 10.1016/j.cherd.2013.08.018.
- Shang, G. *et al.* (2013) 'Kinetics and mechanisms of hydrogen sulfide adsorption by biochars', *Bioresource Technology*. Elsevier Ltd, 133, pp. 495–499. doi: 10.1016/j.biortech.2013.01.114.
- Shang, G. *et al.* (2016) 'Adsorption of hydrogen sulfide by biochars derived from pyrolysis of different agricultural/forestry wastes', *Journal of the Air and Waste Management Association*. Taylor & Francis, 66(1), pp. 8–16. doi: 10.1080/10962247.2015.1094429.
- Siepmann, J., Siegel, R. A. and Rathbone, M. J. (2012) *Fundamentals and applications of controlled release drug delivery. Fundamentals and Applications of Controlled Release Drug Delivery*. doi: 10.1007/978-1-4614-0881-9.
- Simonin, J. P. (2016) 'On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics', *Chemical Engineering Journal*. Elsevier B.V., 300, pp. 254–263. doi: 10.1016/j.cej.2016.04.079.
- Skerman, A. G. *et al.* (2017) 'Low-cost filter media for removal of hydrogen sulphide from piggery biogas', *Process Safety and Environmental Protection*. Institution of Chemical Engineers, 105, pp. 117–126. doi: 10.1016/j.psep.2016.11.001.
- Sun Choo, H. *et al.* (2013) 'HYDROGEN SULFIDE ADSORPTION BY ALKALINE IMPREGNATED COCONUT SHELL ACTIVATED CARBON Abbreviations BET Brunauer-Emmett-Teller CSAC Coconut shell activated carbon IAC Impregnated activated carbon POME Palm oil mill effluent SEM Scanning electron microscopy', *Journal of Engineering Science and Technology*, 8(86), pp. 741–753.
- Thilagan, J., Gopalakrishnan, S. and Kannadasan, T. (2013) 'A study on Adsorption of Copper (II) Ions in Aqueous Solution by Chitosan - Cellulose Beads Cross Linked by Formaldehyde', 2(Ii), pp. 1043–1054.
- Yan, R. *et al.* (2002) 'Kinetics and mechanisms of H₂S adsorption by alkaline activated carbon', *Environmental Science and Technology*, 36(20), pp. 4460–4466. doi: 10.1021/es0205840.
- Zulkefli, N. N. *et al.* (2017) 'Mathematical modelling and simulation on the adsorption of Hydrogen Sulfide (H₂S) gas', *IOP Conference Series: Materials Science and Engineering*, 206(1). doi: 10.1088/1757-899X/206/1/012069.