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# Modeling and Optimization for H<sub>2</sub>S Adsorption from Wastewater Using Coconut Shell Based Activated Carbon

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### ABSTRACT

In the current work, the Response Surface Method (RSM) is used to optimize the adsorption efficiency of hydrogen sulfide (H<sub>2</sub>S) onto the coconut shell activated carbon. The considered design (or operating) variables are; initial H<sub>2</sub>S concentration, adsorption contact time and adsorbent dosage, while the response variable is H<sub>2</sub>S equilibrium concentration (Ce). Coconut shell is an agricultural by-product in Malaysia, which could be used as a source of carbon. The combination of the operating variables was determined based on the 2<sup>3</sup> factorial experimental design method. On the other hand, SEM, EDX and FTIR techniques were utilized to investigate the physical and chemical properties of the prepared activated carbon. H<sub>2</sub>S removal efficiency was investigated using batch mode process. It was found that the adsorption contact time and the initial H<sub>2</sub>S concentration play a dominant role in affecting the adsorption process. Moreover, the ANOVA test showed that the model is significant. It is observed that the H<sub>2</sub>S adsorption rate can be better represented by the pseudo-first-order model as compared to the second order model. The isotherm adsorption mechanism models are also investigated in the current work. Freundlich model was found to be the well fitted adsorption process model. The study revealed that, coconut shell based activated carbon is a good candidate adsorbent for removing dissolved H<sub>2</sub>S from synthetic petrochemical refinery wastewater.

### INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) is an extremely lethal and destructive substance; however, it is extensively produced as a by-product in many industries, such as the petroleum refineries. Wastewater produced from petroleum refineries contains risky substances such as H<sub>2</sub>S. H<sub>2</sub>S could shape corrosive rain and destruct the ozone layer (Cheng *et al.* 2012). Besides that, H<sub>2</sub>S can corrode metals and even concretes (Vollertsen *et al.* 2008). The most essential type of sulfur is H<sub>2</sub>S. Other components such as bisulfide (HS<sup>-</sup>) and sulfide (S<sup>2-</sup>) may exist and they may volatilize to become H<sub>2</sub>S gas (Chaudhuri 2004). It depletes the dissolved oxygen in a biological system which is detrimental to the benthic aquatic lives. Various ways have been proposed in order to remove the dissolved H<sub>2</sub>S before the wastewater is released to the environment, including precipitation (Ma *et al.* 2006), reduction (Montes *et al.* 2012), oxidation (Diez *et al.* 2014) and adsorption (Cheng *et al.* 2012). Both oxidation and adsorption methods have been successfully employed. The metal based oxide catalysts used so far include like vanadium (Shin *et al.* 2001), iron (Li *et al.* 1997), titanium (Chun *et al.* 1998), and chromium (Uhm *et al.* 1999). On the

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other hand, the adsorption of H<sub>2</sub>S onto an activated carbon has been observed to be the best method amongst the strategies mentioned above due to its efficiency in adsorbing a wide scope of adsorbates and its operational simplicity. However, it is important to note that economically accessible activated carbons are costly (Chakraborty *et al.* 2005); therefore, scientists have created activated carbons from agricultural wastes such as cassava peel (Sivakumar *et al.* 2001), oil-palm shell (Guo *et al.* 2007), carbon steel slag (Asaoka *et al.* 2013), coffee industry waste materials (Nowicki *et al.* 2014), sawdust pellets (Kazmierczak-Razna *et al.* 2015), wood (Adib *et al.* 1999), sewage sludge and pig manure (Xu *et al.* 2014). In the current work, we have used coconut shell as a source of carbon due to its abundance in Malaysia. Both physical and chemical activation methods are used to activate the carbon by employing activation agents such as KOH and CO<sub>2</sub>. In order to find the best combination of the operating variables affecting the adsorption rate of H<sub>2</sub>S, the Response Surface Method (RSM), which is already implemented in the commercial software called Design of Expert (DOE), is used. It was used due to the lack of conventional and classical methods of studying a process by changing one variable at a time and maintaining other factors of the process at a constant level. In addition to that, it does not describe the combined impact of all variables included. Moreover, it requires substantial number of experiments and time consuming to decide optimum levels, which are questionable. Thus, the experimental work conducted by experiment design technique which was used as a useful statistical model tool which enables comprehension of optimum parameters to obtain the optimum conditions for adsorption of H<sub>2</sub>S by using coconut shell based activated carbon (ACCNS). RSM is firstly proposed by Box and Wilson (Box and Wilson 1951) and it can be utilized to evaluate the relative significance of several influencing variables even in the presence of complex interactions. (Hounsa *et al.* 1996). In the current work, the main objective is to determine the optimum operating conditions needed to maximize the adsorption rate of dissolved H<sub>2</sub>S from wastewater by using coconut shell as the of activated carbon. Also, the mechanisms of adsorption process are identified in this study by using isotherm and kinetic models.

## MATERIALS AND METHODS

### *Preparation of activated carbon:*

Coconut shells were collected from an agriculture area near Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia. The shell was cleaned and soaked in hot water to remove dirt and impurities. It was subsequently dried and grinded to small pieces (0.5–1 mm). The pre-treated sample was carbonized at 700 °C with heating rate of 10 °C/min (first pyrolysis) in a horizontal tubular reactor placed in a tube furnace. The char produced was then drenched in potassium hydroxide (KOH) solution with an impregnation proportion of 4:1 for 24 h. The carbon produced was blended with KOH pellets with various Impregnation Proportion (IR) defined as:

$$IR = \frac{W_{KOH}}{W_c} \quad (1)$$

where W<sub>KOH</sub> is the weight of KOH pellets (g) and W<sub>c</sub> is the weight of carbon (g). Distillate water was then added to dissolve all the KOH pellets. The impregnation was then dried in an oven overnight at 105 °C and activated by utilizing the heating rate of 10 °C/min (via injecting the decontaminated nitrogen (99.995%) with flow rate of 150 cm<sup>3</sup>/min for 2 h). Upon reaching the temperature of 750 °C, the N<sub>2</sub> gas was switched to CO<sub>2</sub> gas for activation process. The activated product was then cooled to room temperature under nitrogen flow rate of 150 cm<sup>3</sup>/min, which was then washed by hot distillate water and 0.1 M HCl until the pH value of the washing solution becomes 6.0–7.0.

### *The physical characterization measurements:*

The pH of ACCNS surface was measured via mixing a 0.4 g of dry ACCNS sample with 20 mL of water. The mixture was stirred for 12 h to achieve equilibrium. Then, the pH of the suspension was measured. The surface morphology of the sample was examined by utilizing the Scanning Electron Microscope (SEM). The SEM was conducted using a HITACHI S-3400N system at an accelerating potential of 20 kV. Elemental analysis or chemical characterization of samples was conducted by utilizing Energy-Dispersive X-ray spectroscopy (EDX). The Fourier Transform Infrared Spectroscopy (FTIR) was used to examine the functional groups on the surface of modified samples. FTIR spectra were recorded between 4000 and 400 cm<sup>-1</sup>.

### *Preparation of Hydrogen Sulfide solution:*

In this work, the synthetic waste water was prepared in accordance with the procedure outlined by Asaoka (Asaoka *et al.* 2009). An aliquot of Na<sub>2</sub>S.9H<sub>2</sub>O was dissolved in 500 mL, 0.01 M KCl solution purged with N<sub>2</sub> gas. The mixture was subsequently neutralized by using 0.2 M HCl. H<sub>2</sub>S could dissolve in water around 4-6 g/L (Heinonen 2012).

**Batch equilibrium studies:**

In order to examine the adsorption behaviour of ACCNS, the H<sub>2</sub>S concentration was initially measured. Batch process mode was used to test the removal efficiency of H<sub>2</sub>S. The adsorption conditions were carried out by degassing the mixture at 105 °C for 24 h in the oven. The pH of the mixture was changed to 7.0, which was subsequently agitated by using an electric shaker (150 rpm) performed at 30 °C for 14 hours to investigate removal efficiency of H<sub>2</sub>S from synthetic wastewater. Equation (2) is used to determine the adsorption capacity ( $q_e$ , mg/g) defined as:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $V$  is the solution volume (L),  $m$  is the adsorbent amount (g),  $C_0$  and  $C_e$  are the initial and final concentrations in the pollutants, respectively. All the experimental measurements were done at fume hood as H<sub>2</sub>S is a very dangerous gas. The sample yield is calculated via the following relation:

$$Yield (\%) = \frac{W_c}{W_o} \times 100 \quad (3)$$

where  $W_c$  and  $W_o$  are the dry weight of final sample (g) and the dry weight of precursor (g), respectively. The removal percentage (RE, %) can then be defined as:

$$RE (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (4)$$

where  $C_0$  is initial concentration of solute (mg/L),  $C_e$  is equilibrium concentration of solute (mg/L),  $V$  is volume of solution (L) and  $m$  is mass of activated carbon used (g).

**Optimization and Modelling:****Design of experiments:**

Response Surface Method (RSM) is beneficial in demonstrating a response of interest is impacted by a few operating variables (Montgomery 2001). Practically, these operating variables are subjected to the corresponding design constraints and the combinations of these operating variables (which is important for the design of experiment) can be obtained via the Central Composite Design (CCD). Generally, CCD consists of a 2<sup>n</sup> factorial runs with 2<sup>n</sup> axial runs and n<sup>c</sup> center runs (six replicates).

In the current work, the operating variables that might affect the adsorption rate of H<sub>2</sub>S are (i) adsorption contact time; (ii) H<sub>2</sub>S initial concentration and (iii) adsorbent dosage. The sequence of the experiment is randomized in order to minimize the effects due to uncontrolled factors. In the current RSM study, we are interested in looking at the final response, i.e. the equilibrium concentration of H<sub>2</sub>S ( $C_e$ ). An empirical model correlating the response and the operating variables can then be defined based on the second degree polynomial (Zainudin *et al.* 2005):

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left( \sum_{i=1}^n b_{ii} x_i^2 \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (5)$$

where  $Y$  is the predicted response,  $b_0$  is the constant coefficient,  $b_i$  is the linear coefficient,  $b_{ij}$  is the interaction coefficient,  $b_{ii}$  is the quadratic coefficients and  $x_i, x_j$  are the coded values of the independents process variables.

**Statistical and Graphical Analysis:**

The significance of the model equations and their terms can be assessed by utilizing coefficient of determination ( $R$ -squared), Fisher esteem ( $F$ -esteem), likelihood ( $P$ -quality), and residual (Hassani *et al.* 2014). 3D plots are generated to examine the impact of operating variables on the response.

**Optimization:**

The lower-upper constraints of the operating variables such as adsorption contact time (A), H<sub>2</sub>S initial concentration (B) and adsorbent dosage (C) are prescribed as 100–500 mg/L, 360–720 min, and 0.1–1 g, respectively. Here, we intend to minimize the response variable ( $Y_1$ ), i.e. H<sub>2</sub>S concentration at equilibrium (mg/L).

**Software Application:**

The commercial software, i.e. the Design of Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) is utilized for the test, regression, graphical analysis, optimization, and statistical investigation on the equation developed (see Equation 5).

**Adsorption isotherm models:**

The adsorption isotherm relates the amount of adsorbate per unit mass of adsorbent at steady temperature and the concentration of adsorbate at equilibrium condition. Two isotherm models are considered here, i.e. Langmuir isotherm and Freundlich isotherm.

**Langmuir isotherm:**

The Langmuir isotherm relates to homogeneous adsorption, where every particle shows steady enthalpy and sorption enactment vitality (T. W. Weber and Chakravorti 1974). The linear Langmuir isotherm model is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0}\right) C_e \quad (6)$$

where  $C_e$  is the equilibrium concentration of the adsorbate ( $H_2S$ ) (mg/L),  $q_e$  is the measure of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $Q_0$  and  $b$  are Langmuir constants identified from monolayer adsorption limit and proclivity of adsorbent towards adsorbate, respectively. The dimensionless equilibrium parameter ( $R_L$ ) can be characterized as below equation (Abdel Ghafar *et al.* 2015).

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial hydrogen sulfide concentration (mg/L). The  $R_L$  value shows the state of the isotherm, i.e. unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) (Bello *et al.* 2008).

**Freundlich isotherm:**

In contrast with Langmuir isotherm model, the Freundlich isotherm supports heterogeneous surface energies, where the vitality term in the Langmuir condition changes as a component of surface scope (W. J. Weber 1972). The incline is ranging between 0 and 1, which is used to measure the adsorption force or surface heterogeneity. The parameter  $1/n$  of  $> 1$  signifies agreeable adsorption (Haghsereht and Lu 1998) ; (Foo and Hameed 2010). The Freundlich model can be written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

where  $C_e$  is the equilibrium concentration of the adsorbate ( $H_2S$ ), and  $K_F$  and  $n$  are Freundlich constants.

**Batch kinetic studies:**

Adsorption kinetic study is performed to reproduce the adsorption of  $H_2S$  by adsorbents. Aqueous samples have been taken at prescribed time intervals. The amount adsorbed at time  $t$ ,  $q_t$  (mg/g), is computed via:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (9)$$

where  $C_t$  (mg/L) is the liquid concentration of  $H_2S$  at time  $t$ . Kinetic data is then fitted by utilizing the pseudo-first-order and the pseudo-second-order models. In order to explore the adsorption kinetics of  $H_2S$  on adsorbents, these two models are utilized to simulate the experimental data.

**Pseudo-first-order kinetic model:**

Normally, the pseudo-first-order kinetic model is used to simulate adsorption kinetics. The rate constant for adsorption is resolved from the pseudo-first-order equation as given by Lagergren and Svenska (Lagergren 1898); (Agarwal *et al.* 2016):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

where  $q_e$  and  $q_t$  are the  $H_2S$  adsorbed (mg/g) at equilibrium and at time  $t$  (h), respectively, and  $k_1$  is the rate constant of adsorption ( $h^{-1}$ ).  $k_1$  is calculated from the plots of  $\ln(q_e - q_t)$  against  $t$  for various  $H_2S$  concentrations.

**Pseudo-second-order kinetic model:**

A pseudo-second-order equation based on equilibrium adsorption (Ho and McKay 1998) can be expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \quad (11)$$

where  $k_2$  (g/mg h) is the rate constant for second-order adsorption.

Validity of kinetic model

Other than the  $R^2$ , the validity of a kinetic model is confirmed by the aggregate of error squares (SSE, %), written as:

$$SSE(\%) = \sqrt{\frac{\sum(q_{e,exp} - q_{e,cal})^2}{N}} \quad (12)$$

where  $N$  is the number of data points. Here,  $q_{exp}$  and  $q_{cal}$  (mg/g) are the experimental and calculated adsorption capacities, respectively. Good fitting is obtained if the  $R_2$  value is  $\sim 1$  and  $SSE \sim 0$ .

## RESULTS AND DISCUSSION

### Physical characterization of ACCNS:

The relatively high porosity observed in ACCNS is beneficial in adsorption. SEM, EDX, and FTIR are useful in determining the porosity, the composition and the functional groups on the surface of the ACCNS. From Fig. 1, it can be clearly seen high number of large pores in the sample with indicates the high porosity of ACCNS, making it attractive for  $H_2S$  removal. It is obvious that carbon is the most dominant component in ACCNS as it shown from EDX plot in Fig. 2. Table 1 reports the elemental composition of the adsorbent. The FTIR spectrum of ACCNS is displayed in Fig. 3. Here, the prepared activated carbon displays the following bands, i.e.  $1680\text{ cm}^{-1}$ : C=C for alkene groups,  $2020\text{ cm}^{-1}$ : C=N nitriles groups and  $2160\text{ cm}^{-1}$ : C=C acetylene.

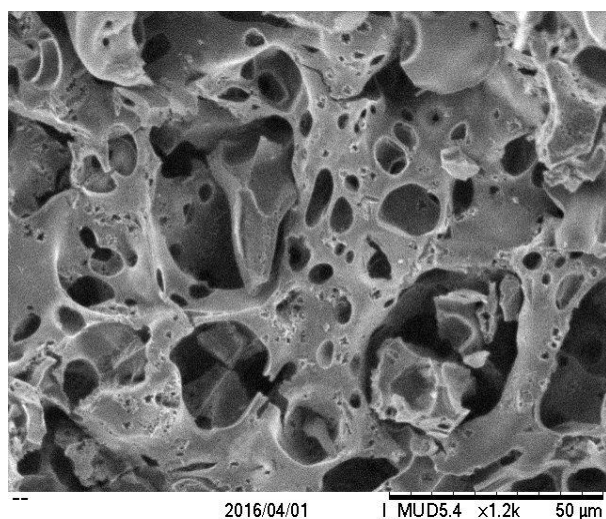


Fig. 1: SEM image of ACCNS.

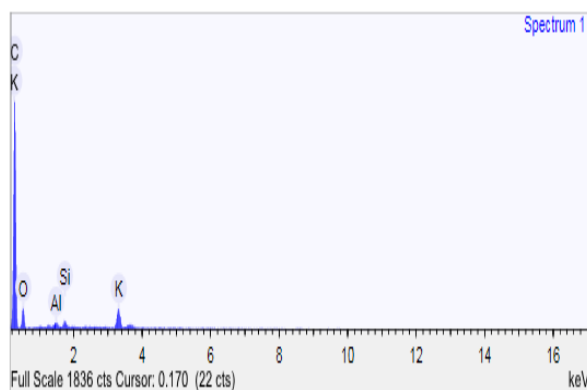
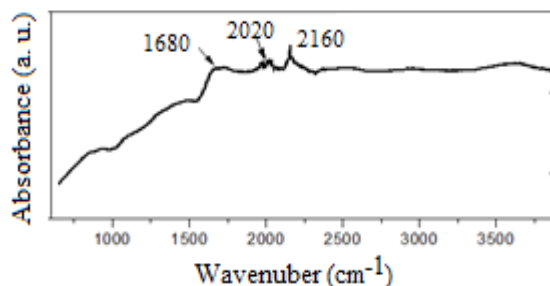


Fig. 2: EDX of fresh ACCNS.

**Table 1:** The elemental composition for the fresh adsorbent.

Element	Weight (%)
Carbon	76.648
Oxygen	19.195
Aluminum	0.356
Silicon	0.574
Potassium	3.227

**Fig. 3:** FTIR spectrum of ACCNS.**Responses obtained from the experiment:**

The design matrix of the current experimentation is shown in Table 2. From the results, the lowest  $C_e$  of 0.5 mg/L is obtained at run6. Table 3 shows the regression statistics for different models. It shows that the  $R^2$  value is the lowest for linear model. Meanwhile, the quadratic model reports a smaller standard deviation of 3.66 and a relatively high predicted  $R^2$  (0.8689). Therefore, the quadratic model is suggested by the software and the cubic model is aliased.

**Table 2:** Experimental design matrix and results.

Runs	H <sub>2</sub> S removal variables			C <sub>e</sub> (mg/L)
	A: Contact time (min)	B: Initial H <sub>2</sub> S concentration (mg/L)	C: Adsorbent dosage (g)	
1	360	100	0.10	6.0
2	720	100	0.10	5.0
3	360	500	0.10	78
4	720	500	0.10	35.0
5	360	100	1.00	3.2
6	720	100	1.00	0.5
7	360	500	1.00	55.0
8	720	500	1.00	0.6
9	360	300	0.55	23.0
10	720	300	0.55	0.9
11	540	100	0.55	6.5
12	540	500	0.55	62.0
13	540	300	0.10	18.0
14	540	300	1.00	1.5
15	540	300	0.55	15.5
16	540	300	0.55	15.0
17	540	300	0.55	15.5
18	540	300	0.55	16.0
19	540	300	0.55	17.0
20	540	300	0.55	15.5

**Table 3:** Regression statistics for concentration at equilibrium.

Source	Standard deviation	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	Comment
Linear	12.42	0.7278	0.6768	0.4579	
2FI	8.97	0.8847	0.8314	0.6777	
Quadratic	3.66	0.9853	0.9720	0.8689	Suggested
Cubic	0.76	0.9996	0.9988	0.8473	Aliased

**Development of regression model equation:**

Centre composite design CCD was using of the Design Expert software to developed the correlation between the response surface and factors. Relationship coefficient and standard deviation were utilized to assess the wellness of the models developed. As indicated by successive model aggregate of squares, the models were chosen in view of the most astounding request polynomials where the extra terms were noteworthy and the models were not associated (Chaudhary and Balomajumder 2014), (Tan, Ahmad, and Hameed 2008). The smaller the standard

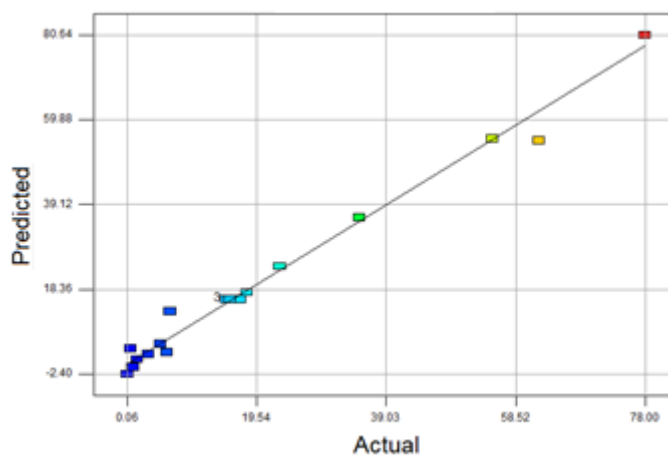
deviation and the closer the  $R^2$  value is to unity, the better the model in predicting the response (Alam *et al.* 2009). The quadratic model suggested by the software can be written as:

$$C_e = 15.98 - 12.37A + 20.97B - 8.17C - 11.67AB - 1.70AC - 6.22BC - 4.38A^2 + 17.92B^2 - 6.58C^2 \quad (13)$$

ANOVA is subsequently performed and the results are tabulated in Table 4. Table 4 shows that the quadratic model has the  $F$ -value of 74.27, indicating that the model is significant. Also, model terms are significant if they exhibit  $P$  value of less than 0.05 (Basu, Monal, and Pinaki 2012). Therefore, the significant model terms are A, B, C, AB, BC,  $B^2$ , and  $C^2$ , while AC, and  $A^2$  are the insignificant model terms. As noted from Table 3, the standard deviation of Eq. (13) is 3.66. The error of estimation might be due to other parameters (apart from A, B and C) affecting the  $H_2S$  removal. Further investigations are needed to verify this hypothesis. Fig. 4 compares  $C_e$  values obtained from the experiment as well as the model equation. As expected, the experimental values are quite close to the predicted values, indicating that the model developed is successful. However, some inaccuracies are observed as the  $C_e$  is low. This is due to the low  $R^2$  and high standard deviation values of the model as explained earlier.

**Table 4:** ANOVA table for removal efficiency (model for response  $C_e$ )

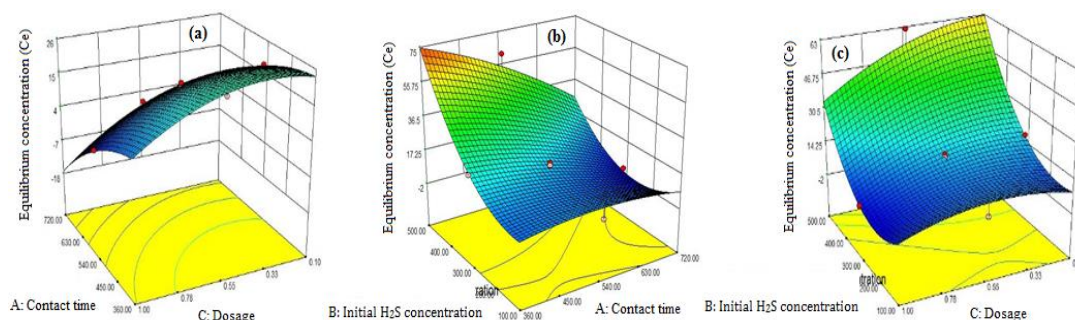
Sources	Sum of squares	df	Mean square	F-value	P-value	Comment
Model	8932.65	9	992.52	74.27	< 0.0001	significant
A	1531.16	1	1531.16	114.58	< 0.0001	significant
B	4399.09	1	4399.09	329.19	< 0.0001	significant
C	668.14	1	668.14	50.00	< 0.0001	significant
AB	1089.51	1	1089.51	81.53	< 0.0001	significant
AC	23.26	1	23.26	1.74	0.2165	insignificant
BC	309.51	1	309.51	23.16	0.0007	significant
A <sup>2</sup>	52.84	1	52.84	3.95	0.0748	insignificant
B <sup>2</sup>	882.74	1	882.74	66.06	< 0.0001	significant
C <sup>2</sup>	119.20	1	119.20	8.92	0.0137	significant
Residual	133.63	10	13.36			
Lack of Fit	131.26	5	26.25	55.27	0.0002	significant



**Fig. 4:** The experimental and predicted values of variables for removal  $H_2S$ .

#### **Combined effect of factors on response:**

The combined effect of contact time and adsorbent dosage on  $C_e$  at constant initial concentration is shown in Fig. 5a. However, the combined effect of contact time and initial concentration at constant adsorbent dosage shown in Fig. 5b demonstrates that both initial  $H_2S$  concentration and adsorption contact time have exhibited little combined effect on  $C_e$ . It is observed that the effect of initial  $H_2S$  concentration is relatively higher than that of the adsorption contact time and increase in initial  $H_2S$  concentration would correspondingly increase  $C_e$ . The combined effect of initial concentration and adsorbent dosage at constant contact time is shown in Fig. 5c. It demonstrates that the initial concentration and the adsorbent dosage have insignificant combined effect on  $C_e$ . Also, the initial concentration exhibits greater effect on  $C_e$ .



**Fig. 5:** Combined effect of contact time and adsorbent dosage (a), contact time and initial H<sub>2</sub>S concentration (b) and initial concentration and adsorbent dosage (c) on  $C_e$ .

#### Optimization:

From the software, the optimum operation conditions leading to the minimum concentration of H<sub>2</sub>S at equilibrium are:

- A- Adsorption contact time = 360 min.
- B- Initial H<sub>2</sub>S concentration = 131 mg/L.
- C- Adsorbent dosage = 1.0 g.

#### Model validation:

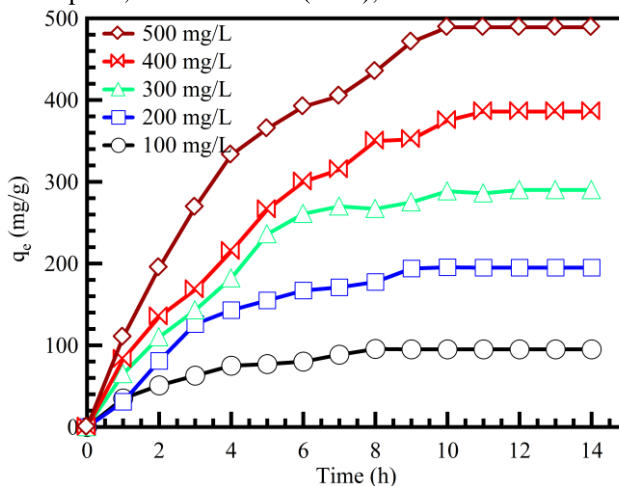
An experiment is then performed using the parameters suggested by the design of experiments. The results are listed in Table 5. It is found that the experimental  $C_e$  value compares well with the RSM model equation. The percentage error is only 2.65%. Therefore, the model equation suggested by RSM is valid and can be used to predict the response variable  $C_e$  accurately.

**Table 5:** Model validation

Variables			Experimental	Theoretical	Error (%)
T (min)	$C_o$ (mg/L)	Dosage (g)	$C_e$ (mg/g)	$C_e$ (mg/L)	
360	131	1	1.02	0.983	2.65

#### Effect of contact time and initial H<sub>2</sub>S concentration on adsorption equilibrium:

Commonly, there are numerous variables affecting the adsorption limit of H<sub>2</sub>S. For example, from Fig. 6, adsorbent capacity at a particular time instant increases with respect to the initial H<sub>2</sub>S concentration. The contact times required to achieve equilibrium for initial H<sub>2</sub>S concentrations of 100–500 mg/L are ranging from 8 to 12 h. In the current study, the required information is measured at 14 h to ensure that a complete equilibrium is achieved. For cases involving low initial H<sub>2</sub>S concentrations, the rate of adsorbent capacity is relatively mild as compared to those involving high initial H<sub>2</sub>S concentrations. However, the initial rate of adsorbent capacity is high for all cases, and the capacity reaches a plateau (equilibrium) after a certain period. The time required to reach equilibrium is lower if the initial H<sub>2</sub>S concentration is lower, mainly due to the abundance of voids (thanks to porosity) in trapping the H<sub>2</sub>S molecules. Also, several active functional groups are available on the adsorbent surface at the beginning of adsorption, such as nitriles (C=N), which would in turn enhance the adsorption.

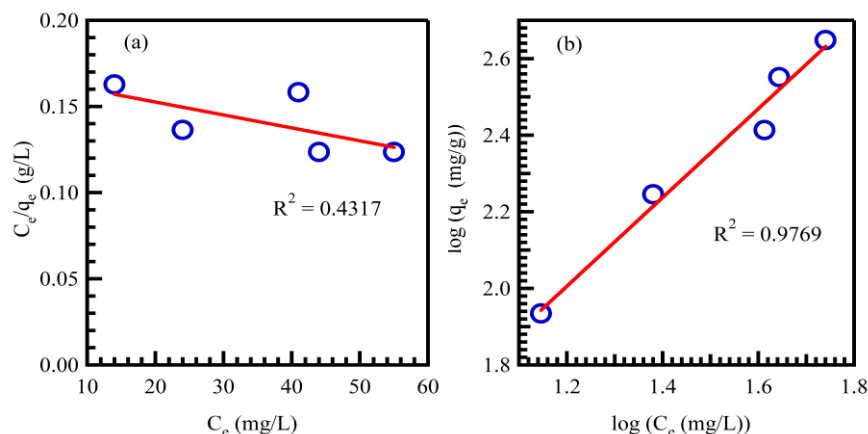


**Fig. 6:** Variation of adsorption capacity with adsorption time at various initial H<sub>2</sub>S concentration.



### Adsorption isotherms:

For the Langmuir isotherm, the straight line with an incline of  $1/Q_0$  was gotten from the plot of  $C_e/q_e$  against  $C_e$  (Fig. 7a). The Langmuir constants  $b$  and  $Q_0$  were calculated from Eq. (6), which are appeared in Table 6. The Langmuir and the Freundlich isotherm models are compared in this section. From Fig. 7a, it is found that the Langmuir adsorption isotherm model is not appropriate in describing the adsorption of  $H_2S$  on ACCNS. The  $R^2$  value is merely 0.4317, indicating that the fitting is poor. However, by examining Fig. 7b, the fitting error of the Freundlich isotherm is relatively small as compared to that of the Langmuir model, reporting the  $R^2$  value of 0.9769. The parameters used in both isotherm models are tabulated in Table 6.



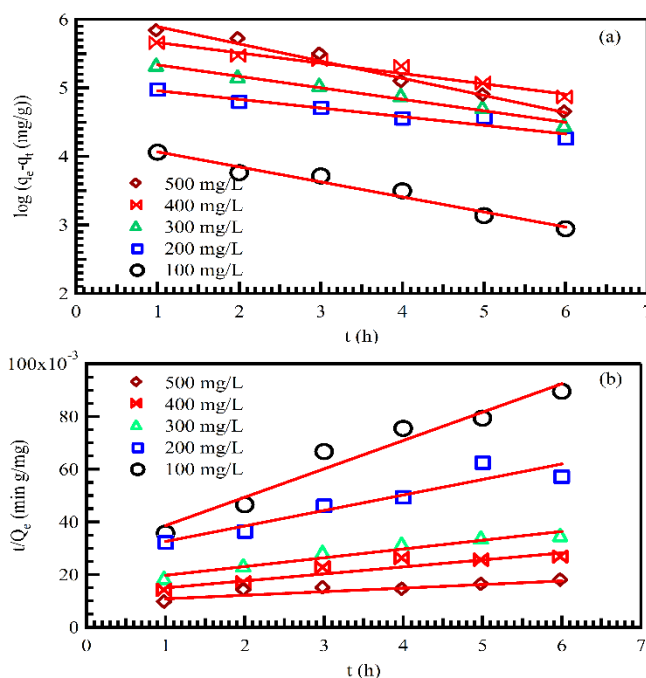
**Fig. 7:** Langmuir (a) and Freundlich (b) adsorption isotherm model of  $H_2S$  on ACCNS at 30 °C.

**Table 6:** Langmuir, and Freundlich isotherm model parameters and correlation coefficients for the adsorption of  $H_2S$  on ACCNS.

Isotherm models	Concentration (mg/L)	Parameters		$R^2$
		$Q_0$ (mg/g)	$b$ (L/mg)	
Langmuir	500	1333	0.0044	0.4317
		$K_F$ (mg/g (L/mg) <sup>1/n</sup> )	$n$	
Freundlich	500	4.124	0.863	0.9769

### Adsorption kinetics:

Fig. 8a and b show the pseudo-first- and second-order kinetics for the adsorption of hydrogen sulfide on ACCNS, respectively. As seen from Fig. 8a, the predicted values agree considerably well with those measured. Table 7 shows the fitting errors of both the first order and second order kinetics models. As seen, the fitting errors of the second order model are higher for all cases involving various initial  $H_2S$  concentrations.



**Fig. 8:** Pseudo-first-order kinetics (a) and Pseudo-second-order kinetics (b) for the adsorption of  $H_2S$  on ACCNS.

**Table 7:** Pseudo-first-order, pseudo-second-order, kinetic model, and correlation coefficient for the adsorption of H<sub>2</sub>S on ACCNS.

Initial H <sub>2</sub> S concentration (mg/L)	q <sub>e</sub> , exp (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		q <sub>e</sub> , cal (mg/g)	K <sub>1</sub> (1/h)	R <sup>2</sup>	SSE (%)	q <sub>e</sub> , cal (mg/g)	K <sub>2</sub> (g/mg h)	R <sup>2</sup>	SSE (%)
100	86	72.67	0.21926	0.97	5.4	92.94	0.00415	0.95	2.8
200	176	161.7	0.12629	0.93	5.8	169.85	0.001299	0.89	2.5
300	259	245.8	0.16763	0.98	5.3	300.6	0.000673	0.944	16.9
400	356	334.6	0.15063	0.96	8.7	378.5	0.000564	0.866	8.98
500	445	466.9	0.25111	0.98	8.9	738.1	0.000194	0.82	119.6

**Conclusions:**

A full factorial design has been conducted to study the effects of varying three operating variables on the response variable, i.e. the equilibrium concentration of H<sub>2</sub>S (C<sub>e</sub>). A quadratic model has been proposed to relate the operating variables with the response variable. It has been found that the initial concentration and the contact time are more sensitive to C<sub>e</sub> as compared to the adsorbent dosage. The optimal combination of the operating variables has been identified and it has been found that the experimental C<sub>e</sub> (based on these optimized operating variables) agrees considerably well with that predicted by the quadratic model. The optimized operating variables are: adsorption contact time of 360 min, initial H<sub>2</sub>S concentration of 131 mg/L and adsorbent dosage of 1 g, which would result in a C<sub>e</sub> value of 0.98 mg/L. From the SEM image, large and well-developed pores have been found on the surface of the activated carbon. Various functional groups on the prepared activated carbon have been determined from the FTIR results as well. The adsorption process can be better described by the Freundlich model and the pseudo-first-order model. This study recommended that, the activated carbon derived from coconut shell is a good candidate for H<sub>2</sub>S removal and waste water treatments.

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