Application of Response Surface Methodology for optimization of palm kernel shell activated carbon preparation factors for removal of H₂S from industrial wastewater

Omar Abed Habeeb[a,b], Ramesh Kanthasamy[a*], Gomaa A. M. Ali[c,d,e], Rosli Mohd. Yunus[a]

[a]Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Gambang, 26300, Kuantan, Malaysia
[b]North Refinery Company, Ministry of Oil of Iraq, Baiji, Salahaldeen, Iraq
[c]Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Gambang, 26300 Kuantan, Malaysia
[d]Chemistry Department, Faculty of Science, Al–Azhar University, Assiut, 71524, Egypt
[e]Al-Azhar Center of Nanoscience and Applications (ACNA), Al–Azhar University, Assiut, 71524, Egypt

Graphical abstract

Industrial effluent — Palm kernel shell based activated carbon — After adsorption

Abstract

Hydrogen sulfide (H₂S) present in the industrial wastewater can be removed using activated carbon produced from palm kernel shell. In this study, three factors namely activation temperature, impregnation ratio of potassium hydroxide to precursor and activation contact time were investigated for the preparation of activated carbon from palm kernel shell (ACPKS) as an adsorbent toward removal of H₂S from synthetic wastewater using central composite design (CCD). Chemical activation method was used to activate the adsorbent with different conditions using KOH as an activating agent. The batch mode was utilized for studying adsorption process. Two responses (removal efficiency (RE, %) and yield of adsorbent (Y, %) are tested by means of two quadratic models. The results shown that the optimum conditions for ACPKS preparation are activation temperature of 829.4 ℃, KOH to precursor ratio of 3.01 w% and activation time of 85 min with responses of 94.41% RE and 39.4% of ACPKS yield. The study recommended that, ACPKS is the promising adsorbent for removing H₂S from wastewater and other aqueous solutions.

Keywords: Palm kernel shell, hydrogen sulfide, response surface methodology, statistical analysis

Abstrak

Kehadiran hidrogen sulfida (H₂S) dalam air sisa industri boleh dsingkirkan dengan menggunakan karbon teraktif daripada cangkerang biji sawit. Dalam kajian ini, tiga faktor (suhu pengaktifan, nisbah penghamilan kalium hidroksida (KOH) kepada pelopor dan pengaktifan masa sentuhan) telah diselidik untuk persediaan karbon teraktif daripada cangkerang biji sawit (ACPKS) sebagai penjerap terhadap penyingkiran H₂S daripada air sisa sintetik menggunakan reka bentuk komposit tengah (CCD). Kaedah pengaktifan kimia telah digunakan untuk mengaktifkan penjerap dalam pelbagai keadaan yang berbeza menggunakan KOH sebagai agen

pengaktifan. Mod kumpulan telah digunakan untuk mengkaji proses penjerapan. Dua tindak balas (kecekapan penyingkiran (RE, %) dan hasil bahan penjerap (Y, %)) telah diuji dengan melaksanakan dua model kuadratik yang berbeza bagi setiap tindak balas. Hasil kajian menunjukkan bahawa keadaan persediaan optimum untuk persediaan ACPKS adalah pada suhu pengaktifan 829.4 ℃, nisbah KOH kepada pelopor 3.01 w% dan masa pengaktifan 85 minit dengan tindak balas RE sebanyak 94.41% dan hasil ACPKS sebanyak 39.4%. Kajian ini memperakui bahawa, ACPKS adalah penjerap harapan untuk menghapuskan H_2S daripada air sisa dan campuran akueus yang lain.

Kata kunci: Cangkerang biji sawit, hidrogen sulfida, tindak balas metodologi permukaan, analisis statistik

1.0 INTRODUCTION

Hydrogen sulfide (H_2S) is a harmful and putrid compound. It has been broadly delivered as a by-product in many factories. Excess exposure to H_2S might cause both chronic and acute ramifications [1]. As recommended by the Agency for Toxic Substances and Disease (ATSDR) that the minimum inhalation risk level of H_2S are 0.02 ppm [2]. However, a concentration of H_2S ranged between 500ppm to 1000 ppm lead to human death [3]. Therefore, to safeguard the employees, the Occupational Safety and Health Administration (OSHA) has implemented the limit of exposure 20 ppm for the general industry during the workday. Moreover, studies reported that the main targeted of H_2S in human body systems are the kidney and liver [4]. Death can cause by severe exposure to high levels of H_2S [5]. On the other hand, the threat of acid rain is an environmental organization issue that caused by (H_2S) through it dissociated by weather humidity and react with oxygen to produce water soluble sulfuric acid (4-6 g/L) [6]. Moreover, H_2S has economic problem arising from corrosion of metals as well as safety problem posed by its highly flammable nature (even in the low level of H_2S) [7]. Another negative impact, H_2S is one of the main poisons for many industry catalysts, and in addition it is a destructive gas towards pipelines and equipment [8]. So removal of H_2S is necessary because of it is exceptionally hazardous and sway the security, environment and human wellbeing. It is essential to find a suitable technique to deal with ousting H_2S from wastewater before transfer it out to the water bodies turn into the ecological controls concern. The removal of H_2S has been carried out by many methods like magnesium peroxide (MgO_2)[9]. Fe^{2+} and Fe^{3+} ions [10], biofilters [11], electrochemical processes [12] and adsorption [13]. However, the adsorption processes are still widely acceptable among researchers [14]. This is because of adsorption method has advantage of low initial cost, ease of operation, simplicity of design, biodegradability, high efficiency and complete removal of pollutants even from dilute solutions and insensitivity to toxic substances [15-20]. In the past, purification technology by adsorption process using activated carbon has been exceedingly used in water purification production of industrial gases and petrochemical industries [21]. Researchers have been investigated the removal of H_2S by many kinds of adsorbent materials such as zeolite[22], silica [23], alumina [24], and activated carbon [25]. Compared to other adsorbents, activated carbon has more widely used as an adsorbent due to it has the acceptable surface area, porosity and even various functional oxygenated groups. But adsorption operation by using the commercially activated carbon to purify water is not cost effective [26-27]. Therefore, many agricultural wastes rich in lignin and cellulose containing structures such as aldehydes, ketones and alcohols are good adsorbents [28]. Many researchers have studied various low-cost bio adsorbents (agricultural wastes, which are environmentally friendly) such as palm oil shell [29] and different agricultural/forestry wastes [30]. Recently, the cost becomes an important issue among researchers. Low cost activated carbon obtained from carbonaceous wastes become attractive in term of cost and availability and it can be considered as an effective method to remove pollutants from water and air by adsorption. Therefore, the wonderful future of activated carbons creates them very appealing for purification of water [31], gases [32]. Low-cost adsorbent preparation from waste agricultural materials has dual benefits of being economical and environmental friendly process [33]. AC from agricultural wastes have been used in several studies such as palm oil shell [29], nut shell [21], pomelo skin [31], and coffee industry waste [32]. Malaysia is currently the world's largest producer and exporter of palm oil. Therefore, huge amount of wastes are produces from palm oil mill [34]. Palm kernel shell is one of the important biomass materials The AC from palm kernel shell is subjected to either chemical activation or physical activation method. In this study, chemical activation using KOH is employed for preparing high-adsorption-capacity activated carbon from palm kernel shell using Response Surface Method (RSM). RSM is a helpful statistical model apparatus which empowers

cognizance of ideal variables to get the optimum preparation conditions to prepare suitable activated carbon for removal of H_2S. This method was proposed by Box and Wilson [35] and it could be utilized to investigate the effect of factors and the interactions onto responses [36]. The main objective of this work is to investigate the optimum conditions needed for the preparation of ACPKS to maximize the removal efficiency (RE, %) and yield of activated carbon (Y, %) to remove dissolved H_2S from synthetic petroleum wastewater.

2.0 METHODOLOGY

2.1 Raw Material

Palm kernel shell (PKS) waste residue was gotten from United Palm Oil Mill, Nibong Tebal, Malaysia. Firstly, the PKS was washed and dried to remove water. This was followed by mechanical grinding and sieving to get particle sizes of 0.5–1 mm and further drying at 110 °C for 24 h until constant weight was obtained. Then, the precursor of PKS was soaked with KOH for 24h, with the KOH/precursor mass ratios of 2:1- 4:1.

2.2 Preparation of Activated Carbon

The carbonization process was conducted by using the tubular horizontal furnace. The dried sample subjected to a pyrolysis process between 724-1000 °C for a known period with a heating rate of 10 °C/min in an inert atmosphere (N_2 flow of 150 mL/min) for activated carbon production. The activation process of carbon was implemented depended on the suggestion of software. The three parameters investigated were Activation temperatures, amount of KOH to precursor and activation contact time. The ranges were 724–1000 °C, 2:1–4:1 and 60-120 min, respectively which demonstrated in Table 1. The final activated carbon product was labeled as ACPKS. Moreover, the preparation of synthetic wastewater was set up as per the strategy reported by somewhere else[37].

2.3 Modeling and Optimization

2.3.1 Design of Experiment

Response surface methodology is an accumulation of numerical and statistical techniques that are valuable for demonstrating, investigation, analysis and modeling of problems in which a response is affected by a few factors [38]. In the current study, the three preparation factors are implemented based on development quadratic models for responses such as RE (%) and Y (%), as well as investigated the optimum preparation conditions. Central Composite Design (CCD) is a useful tool to study the activation process. It is conducted for fitting a quadratic surface. This tool used to analyze the interaction effect between those parameters, as well

as to optimize the effective parameters with a minimum number of experiments. In general, the CCD consists of a 2k factorial runs with 2k axial or star runs and center runs n_c [38]. The three parameters investigated were Activation temperatures (T), the percentage of KOH to precursor and activation contact time (t) with ranges of 724-1000 °C, 2-4 and 60-120 min, respectively. The responses were RE (%) and Y (%) as seen in Table 1. At the center point were performed six replications. Thus, the suggested required experimental (N) by software is as bellow:

$$N= 2k + 2k + n_c= 23 +2*3 + 6 = 20 \quad\quad (1)$$

The residual error was estimated by replicating the central point. According to the range of each factor, the independent factors are coded to the (-1,1) interval. The low and high levels are coded -1 and +1, respectively. The axial points are located at (±œ,0,0), (0,±œ,0), (0,0,±œ) where œ is the distance of the axial point from the center and makes the design rotatable.

In the current study, the preparation conditions for preparing (ACPKS) by utilizing the CCD. The factors tested were (i) x1, activation temperature (°C); (ii) x2, KOH to precursor and (iii) x3, activation contact time. The outcomes acquired and all design informations of the tests did are appeared in Table 1. To minimize the impacts of the uncontrolled components, the all the tests sequence was randomized. The two responses were RE (%) and Y (%). The responses were utilized to build up an empirical model which correlated the response to the three preparation factors utilizing a second degree polynomial equation as given by Eq. (2) [39]:

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

where Y is the predicted response, b_o the constant coefficient, bi the linear coefficients, bij the interaction coefficients, bii the quadratic coefficients and xi, xj are the coded values of the activated carbon preparation variables.

2.3.2 Graphical Analysis and Statistical

The statistical tools such as coefficient of determination (*R*-squared), probability (*P* value), residual and Fisher value (*F*-value) are considered the indicators of showing significance of the model equations [40 - 41]. However, 3D plot graphs are utilized to investigate the interaction impact of variables on responses.

2.3.3 Optimization and Validation

Optimization strategy was utilized to investigate the optimum preparation conditions for the procedure factors under consideration. To accomplish this, objectives are designed the matrix table for all the

variables in ranges with limitations 724–1000 ℃, 2–4 and 60-120 min for factors activation temperatures, percentage of KOH to precursor and activation time, respectively. For the responses surface, the objective for RE (%) and Y (%) were set "maximize". Subsequently adsorption capacity becomes the objective function or performance index. Moreover, model validation was carried out by conducting batch test under optimum preparation conditions. To evaluate the validity of the model, the model predicted values got compared with experimental values.

Table 1 Three factors central composite design matrix and the values of the responses function

Run	ACPKS preparation condition variables						RE (%)	Yield (%)
	Coded variables			A: Activation temperature (℃)	B: KOH to precursor ratio	C: Activation contact time (min)		
1	-1.000	-1.000	-1.000	724.00	2.00	60.00	86.3	40.5
2	-1.000	-1.000	-1.000	724.00	2.00	60.00	85.9	41
3	1.000	-1.000	-1.000	1000.00	2.00	60.00	85.5	35
4	1.000	-1.000	-1.000	1000.00	2.00	60.00	85.8	35.6
5	-1.000	1.000	-1.000	724.00	4.00	60.00	87	39
6	-1.000	1.000	-1.000	724.00	4.00	60.00	86.7	38.7
7	1.000	1.000	-1.000	1000.00	4.00	60.00	87.7	32.9
8	1.000	1.000	-1.000	1000.00	4.00	60.00	87.5	33
9	-1.000	-1.000	1.000	724.00	2.00	120.00	86	38.1
10	-1.000	-1.000	1.000	724.00	2.00	120.00	86.4	38
11	1.000	-1.000	1.000	1000.00	2.00	120.00	86.5	32
12	1.000	-1.000	1.000	1000.00	2.00	120.00	86.4	31.9
13	-1.000	1.000	1.000	724.00	4.00	120.00	86	38.2
14	-1.000	1.000	1.000	724.00	4.00	120.00	86.4	38
15	1.000	1.000	1.000	1000.00	4.00	120.00	87.7	31.3
16	1.000	1.000	1.000	1000.00	4.00	120.00	88	31
17	-1.682	0.000	0.000	629.91	3.00	90.00	84.5	39
18	-1.682	0.000	0.000	629.91	3.00	90.00	84.6	39.2
19	1.682	0.000	0.000	1094.09	3.00	90.00	86	27.5
20	1.682	0.000	0.000	1094.09	3.00	90.00	86	27.6
21	0.000	-1.682	0.000	862.00	1.32	90.00	87.4	38.4
22	0.000	-1.682	0.000	862.00	1.32	90.00	87.3	38.5
23	0.000	1.682	0.000	862.00	4.68	90.00	90	36.4
24	0.000	1.682	0.000	862.00	4.68	90.00	90.2	36.6
25	0.000	0.000	-1.682	862.00	3.00	39.55	87	39.8
26	0.000	0.000	-1.682	862.00	3.00	39.55	87.3	39.5
27	0.000	0.000	1.682	862.00	3.00	140.45	87	36.5
28	0.000	0.000	1.682	862.00	3.00	140.45	87.2	36.5
29	0.000	0.000	0.000	862.00	3.00	90.00	95	38.5
30	0.000	0.000	0.000	862.00	3.00	90.00	94.5	38.6
31	0.000	0.000	0.000	862.00	3.00	90.00	94.6	38
32	0.000	0.000	0.000	862.00	3.00	90.00	95.3	39.6
33	0.000	0.000	0.000	862.00	3.00	90.00	94	38.3
34	0.000	0.000	0.000	862.00	3.00	90.00	95	38.7

3.0 RESULTS AND DISCUSSION

3.1 CCD Model Analysis and Results

At the beginning of the process of looking optimum conditions is to distinguish the info factors that have the most prominent impact on the experimental responses. Activation temperature (724-1000 ℃), activation mass ratio KOH: Precursor (w%), and activation contact time (60-120 min) are the parameters with responses of RE (%) and Y (%). A mathematical relationship between the responses and the preparation process factors was developing by software to get a polynomial model. A quadratic polynomial model was suggested by software to develop the relationship between factors and responses. The predicted and experimental values for both responses and coded, uncoded preparation factors corresponding to different combinations of selected factors are showed in Table 2 and 3.

In addition, Correlation between the factors and responses surface were improved utilizing CCD. As indicated by the consecutive model sum of squares, the models were chosen in light of the most astounding request polynomials where the additional terms were the models were not aliased and significant [42]. Correlation coefficient and standard deviation were utilized to rectify the fitness of the developed models. The closer the R^2 value is to unity and the, smaller the standard deviation the preferable the model in predicting the response [43]. Table 2 demonstrates that the quadratic model for RE % response which has generally a moderately high R² value of 0.9932 with adjusted R² (0.9907) in reasonable agreement with predicted R² (0.9875) and small standard deviation of 0.32. It was additionally seen on the table that the quadratic model for response RE was not aliased. This suggests that the quadratic model can be utilized to portray the relationship between the interacting factors and response. Table 3 likewise demonstrates that the quadratic model for Y (%) which has generally a moderately high R² value of 0.9913 with adjusted R² (0.9881) in reasonable agreement with predicted R² (0.9838) and small standard deviation of 0.39 and the quadratic model for response Y was not aliased. The relationship between the interacting factors and response Y could be described by implementing the quadratic model.

Table 2 Regression statistics for removal efficiency (RE, %) at equilibrium

Source	Standard deviation	R²	Adjusted R²	Predicted R²	Comment
Linear	3.37	0.0403	-0.0557	-0.0847	
2FI	3.54	0.0480	-0.1636	-0.1728	
Quadratic	**0.32**	**0.9932**	**0.9907**	**0.9875**	**Suggested**
Cubic	0.28	0.9956	0.9927	0.9906	Aliased

Table 3 Regression statistics for adsorbent activated carbon yield (Y, %) at equilibrium

Source	Standard deviation	R²	Adjusted R²	Predicted R²	Comment
Linear	1.77	0.7722	0.7494	0.7146	
2FI	1.83	0.7824	0.7340	0.7135	
Quadratic	**0.39**	**0.9913**	**0.9881**	**0.9838**	**Suggested**
Cubic	0.35	0.9941	0.9903	0.9867	Aliased

3.2 Development of Regression Model Equation

The correlation between the response surface and factors was developed by using CCD. Moreover, the wellness of the models developed could be explained by the standard deviation and Relationship coefficient [42], [44]. Thus, the R^2 values of 0.9932 and 0.9913 estimated that 99.32% and 99.13% of the difference in RE (%) and Y (%)could be attributed to the three factors (A -activation temperature, B- KOH: Precursor activation ratio, C- activation contact time. Therefore, the the quadratic model suggested by the software can be written as [37, 44]:

Removal efficiency (RE, %)

$$RE=94.7+0.34A+0.64B+0.03C+0.33AB+0.2AC-0.16BC-3.34A^2-1.12B^2-2.68C^2 \qquad (3)$$

Adsorbent activated carbon yield (Y, %)

$$Y=38.63-3.21A-0.16B-1.02C+0.16AB-0.21AC+0.44BC-1.93A^2-0.46B^2-0.25C^2 \qquad (4)$$

3.3 Statistical Analysis

The lack-of-fit test for response surface quadratic model for RE (%) and the analysis of variance (ANOVA) are shown in Table 4. From Table 4 can be observed the values of F-value of (391.86) and P-value less than (0.05) which indicated that the quadratic model is significant [41]. From that, could be concluded the significant of others parameters and interactions between them. So, can be seen from Table 4 that A, B, AB, BC, AC, A^2, B^2 and C^2 are significant, while only C is the insignificant model terms.

Table 5 represents the lack-of-fit test for a response surface quadratic model for Y (%) and analysis of variance (ANOVA) values. It shows that the significant of the models for parameters and interaction between parameters. From the *F*-value of (304.60), and P value less than 0.0001can be indicated that the quadratic model is significant [45]. So, from Table 5 can be seen that AB is the insignificant model terms. While the others such as A, B, C, AC, BC, A^2, B^2, and C^2, are significant.

Table 4 Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for RE (%)

Sources	Sum of squares	df	Mean square	F-value	P value	Comment
Model	353.44	9	39.27	391.86	< 0.0001	significant
A-Activation temperature	3.15	1	3.15	31.44	< 0.0001	significant
B-KOH:Carbon ratio	11.15	1	11.15	111.24	< 0.0001	significant
C-Activation contact time	0.025	1	0.025	0.25	0.6197	insignificant
AB	1.69	1	1.69	16.86	0.0004	significant
AC	0.64	1	0.64	6.39	0.0185	significant
BC	0.42	1	0.42	4.22	0.0511	significant
A^2	250.88	1	250.88	2503.34	< 0.0001	significant
B^2	100.95	1	100.95	1007.29	< 0.0001	significant
C^2	162.14	1	162.14	1617.87	< 0.0001	significant
Residual	2.41	24	0.10			
Lack of Fit	0.84	5	0.17	2.03	0.1205	not significant

Table 5 Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for adsorbent activated carbon yield (Y, %.)

Sources	Sum of squares	df	Mean square	F-value	P value	Comment
Model	410.28	9	45.59	304.60	< 0.0001	significant
A-Activation temperature	281.27	1	281.27	1879.36	< 0.0001	significant
B-KOH:Carbon ratio	10.04	1	10.04	67.08	< 0.0001	significant
C-Activation contact time	28.29	1	28.29	189.00	< 0.0001	significant
AB	0.42	1	0.42	2.82	0.1059	insignificant
AC	0.72	1	0.72	4.83	0.0379	significant
BC	3.06	1	3.06	20.46	0.0001	significant
A^2	83.92	1	83.92	560.76	< 0.0001	significant
B^2	4.81	1	4.81	32.16	< 0.0001	significant
C^2	1.41	1	1.41	9.41	0.0053	significant
Residual	3.59	24	0.15			
Lack of Fit	1.60	5	0.32	3.05	0.0347	significant

Figure 1 a and b demonstrates the plots of actual versus predicted values of response RE (%) and the Y (%) values which shows the predicted values are quite close to the experimental values, showing that the successful of the developed model. In addition, the interaction of the three factors is described very well by these response surface model equations.
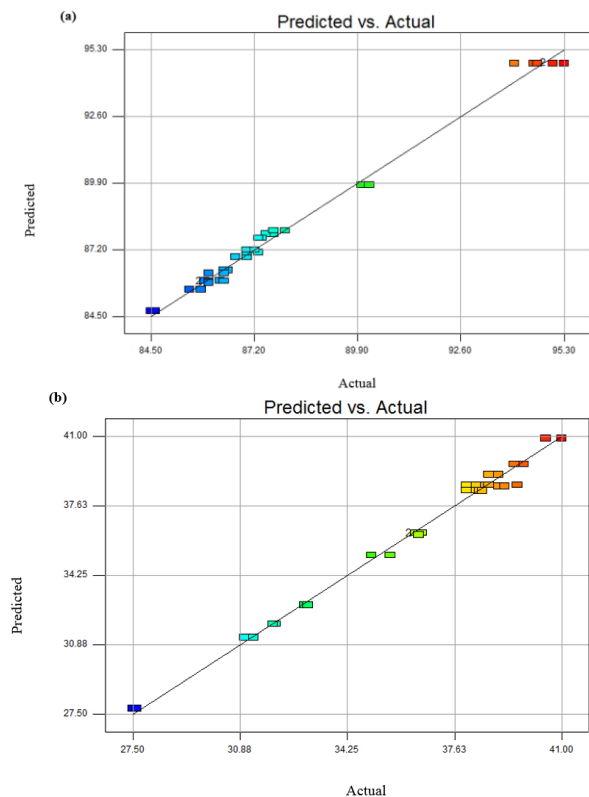

Figure 1 actual and predicted curve for RE (%) (a) and activated carbon yield (Y, %) (b)

3.4 The Interaction Impact of Factors on Response of Removal Efficiency (RE, %)

The 3D graph of the interaction impact of factors such as activation temperature and KOH: Precursor ratio at constant of activation contact time on response R is clearly demonstrated in Figure 2. It shows the clear interactions between these two parameters. The activation temperature with a range between 724 to 1000 ℃ and activation agent mass ratio (KOH: Precursor) with range of (2-4 w%). From Figure 2 it could be noticed that the activation temperature has significant impact on the RE (%) value. At the activation temperature (724 ℃) the effect was very low and it has minimum value of RE % which is around 85.9%. After that, the RE% start increased with increasing the activation temperature until reach the optimum requirement of activation temperature for getting the optimum RE% which around of 829.4 ℃ with RE of 94.41%. After that, rising the activation temperature affected the RE %. This is because of because of the rising activation temperature lead to decreasing the surface area of

the adsorbent and increase the average pore size. Moreover, the higher temperature causes to evaporate the element of potassium (K) due to the boiling point of potassium is 780 ℃. Thus, the number of active sites will be decreased and the percentage of acid/base reaction decreases. Hence, the removal percentage of H_2S is decreasing with increased the activation temperature [46]. Moreover, the activation agent also has important effect on the response RE%. As could be seen from Figure 2 as low the KOH to precursor as low the RE% then the percentage of RE increased when IR increased that mean the chemical activation attributed more on the RE% same trend observed on previous work [47, 48].

More so, the 3D graphs of interaction impact of activation contact time and the activation temperature of AC at constant KOH to precursor on the response of RE (%) are shown in Figure 3. The interaction of activation contact time range (60-120 min) and activation temperature on AC range (724-1000 ℃) have a significant effect on response RE (%). From Figure 3 at the lower values of factors, it is observed that both factors have significant impact on the RE % process at the beginning. However, the effect of the factors increased with increasing activated temperature and activation time until reach the optimum contact time and temperature that required to improve the RE (%) which is around 85 min and 829.4 ℃ respectively. Moreover, both of factors have almost same impact on the response RE % (see Figure 3).

Furthermore, Figure 4 represents the 3D graph of the interaction between activation contact time and KOH to precursor at constant of activation temperature of AC on response RE (%). From Figure 4 it could be noticed that activation contact time has relatively comparable impact with KOH to precursor on response RE%. However, the KOH to precursor has more impact on the RE% as seen in Figure 4. It can be seen from Figure 4 that both of factors have very low RE (%) at (60 min & 2 w%) which is the lower factors values. Thus, the RE (%) start increasing when the factors value increasing until the optimum values that the RE (%) has the higher amount. The activation agent has a specific required time to develop the porosity and burn all the materials that can affect the developed porosity and adsorption capacity of the adsorbent. Similar observation reported by Li, S. *et al*. [46].
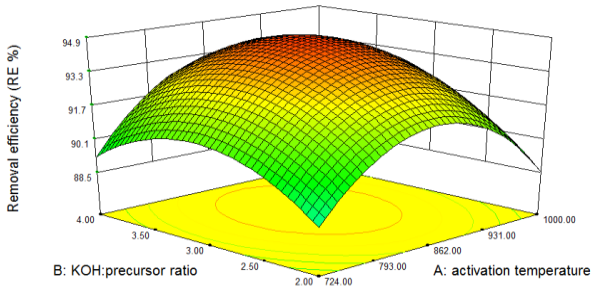
Figure 2 Interaction impact of activation temperature and KOH to precursor ratio at constant activation contact time on response RE (%)
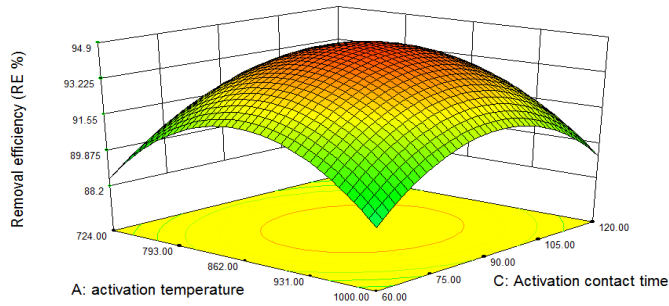

Figure 3 Interaction impact of activation contact time and the activation temperature at constant KOH to precursor ratio on the response of RE (%)
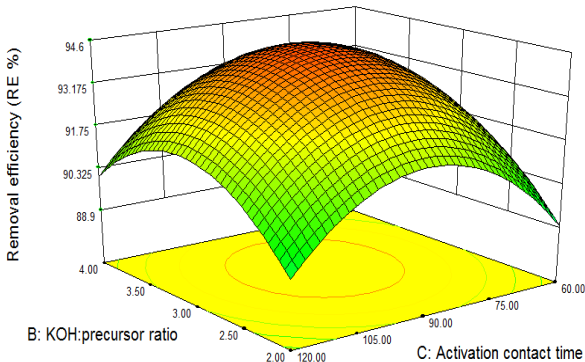

Figure 4 Interaction impact of activation contact time and KOH: precursor ratio at constant activation temperature on response RE (%)

3.5 The Interaction Impact of Factors on Response of Activated Carbon Yield (Y, %)

Figure 5 demonstrated the 3D graph of interaction impact between the KOH: Precursor ratio and the activation temperature of AC on Y (%) at constant of activation contact time. It could be seen from the 3D graph that the factors of activation temperature on AC have the most impact on the response Y (%) compared with the KOH: Precursor ratio factors. The maximum product of AC yield found in the activation temperature around 724 ℃. While the effect of factor of KOH: Precursor ratio was quite smaller (see Figure 5).

In addition, Figure 6 demonstrated the 3D graph of interaction between activation contact time and the activation temperature of AC on Y (%) at constant KOH: Precursor ratio. From Figure 6 it is noticed that the activation temperature of AC has a significant effect on yield (%). So, from Figure 6 could be seen that the optimum activation temperature required for optimum yield around 724 ℃ as demonstrated in Figure 6. On the other hand, during the process as can notice that the impact of factor contact time on response yield was low. Thus, as the contact time value decreased the yield (%) start increased until reach the optimum contact time required to get optimum yield (%) which is around 60 (min).

Finally, the 3D graph of the interaction of activation contact time and KOH: Precursor on AC yield (%) at a constant activation temperature of AC is shown in Figure 7. From that, it noticed that both activation contact time and KOH: Precursor ratio have almost a significant impact on AC yield (%). Both of factors have a very low yield at (120 min & 4 w%) which is the higher factors values. Thus, the AC yield (%) began increasing when the factors values decreasing until reaching the optimum values Y (%).
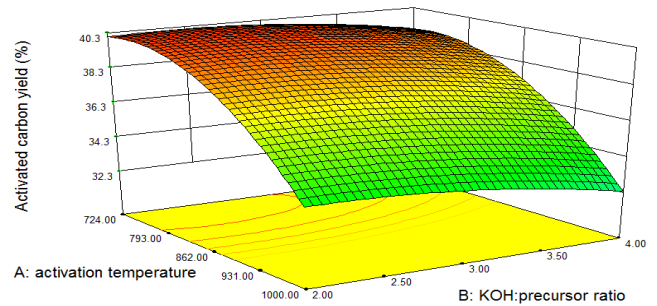

Figure 5 Interaction impact of KOH to precursor ratio and the activation temperature on Y (%) at constant activation contact time
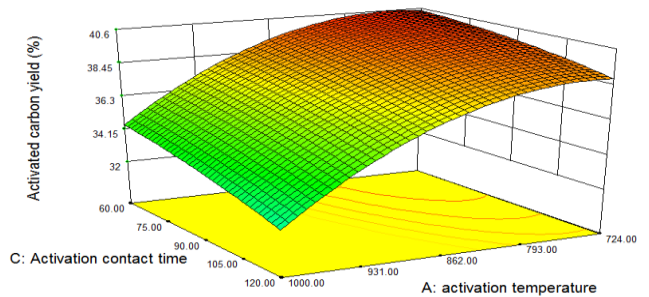

Figure 6 Interaction impact of activation contact time and the activation temperature on Y (%) at constant KOH to precursor ratio
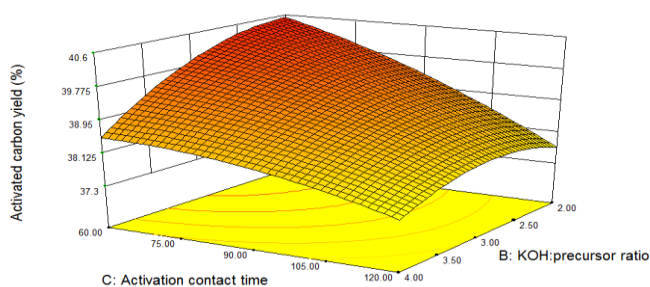
Figure 7 Interaction impact of activation contact time and KOH to precursor ratio on Y (%) at constant activation temperature

3.6 Validation of the Model

The values of responses RE (%) and Y (%) were maximized to get the optimum operation condition for preparing ACPKS. The preparation ACPKS optimum conditions are: activation temperature of 829.4 ℃, KOH: precursor ratio of 3.01 w% and activation contact time of 85 min. The results are listed in Table 6 and found that after repeating the experimental work three times, the predict values was very close to experimental work. It has the percentage error less than (6 %). Thus, the model equation proposed by RSM is valid and could be utilized to predict the responses factors RE and yield accurately.

Table 6 Model validation

Variables			Theoretical		Experimental	
A:Activation temperature (℃)	B: KOH to precursor ratio	C: Activation contact time (min)	RE (%)	Yield (%)	RE (%)	Yield (%)
829.4	3.01	85	94.41	39.4	96	41.2

4.0 CONCLUSIONS

In this study, preparation of activated carbon from palm kernel shell was optimized using central composite design. It was implemented to investigate the impact of activation temperature, impregnation ratio of potassium hydroxide (KOH) to precursor and activation time on the thermal activation process of palm kernel shell. Palm kernel shell is demonstrated to be effective for preparing activated carbon for the removal of H_2S from an aqueous solution. The results of the optimum preparation conditions for the ACPKS were found to be: activation temperature of 829.4 ℃ with KOH to precursor ratio of 3.01 w% and activation time of 85 min with responses of RE and yield of 94.41% and 39.4% respectively. The batch mode was utilized for studying adsorption process. The result found that the ACPKS could be the promising adsorbent for removing H_2S from wastewater.

Acknowledgement

References

[1]   Lambert, T. W., Goodwin, V. M., Stefani, D. 2006. Strosher L. Hydrogen Sulfide (H_2S) and Sour Gas Effects on the Eye. A Historical Perspective. *Sci Total Environ*. 367: 1-22.

[2]   ATSDR. 2008. Minimal Risk Levels (MRLs) for Hazardous Substances. Agency for Toxic Substances and Disease Registry.URL: http://www.atsdr.cdc.gov/mrls/.

[3]   EPA. 2003. Toxicological Review of Hydrogen Sulfide. URL: www.epa.gov/iris.

[4]   Guidotti, T. L. 1994. Occupational Exposure to Hydrogen Sulfide in the Sour Gas Industry: Some Unresolved Issues. *Int Arch Occup Environ Health*. 66: 153-160.

[5]   Hendrickson, R. G., Chang, A., Hamilton, R. J. 2004. Co-worker Fatalities from Hydrogen Sulfide. *Am J Ind Med*. 45: 346-350.

[6]   Heinonen, A. 2012. Adsorption of Hydrogen Sulfide by Modified Cellulose Nano/microcrystals.

[7]   Ozekmekci, M., Salkic, G., Fellah, M. F. 2015. Use of Zeolites for the Removal of H_2S: A Mini-review. *Fuel Process Technol*. 139: 49-60.

[8]   Chen, Q., Wang, J., Liu, X., Li, Z., Qiao, W., Long, D. 2011. Structure-dependent Catalytic Oxidation of H_2S over Na_2CO_3 Impregnated Carbon Aerogels. *Microporous Mesoporous Mater*.142: 641-648.

[9]   Chang Y-J, Chang Y-T, Chen H-J. 2007. A Method for Controlling Hydrogen Sulfide in Water by Adding Solid Phase Oxygen. *Bioresour Technol*. 98: 478-483.

[10] Altaş L, Büyükgüngör H. 2008. Sulfide Removal in Petroleum Refinery Wastewater by Chemical Precipitation. *J Hazard Mater*. 153: 462-469.

[11] Rehman, Z. U., Farooqi, I. H., Ayub, S. 2010. Performance of Biofilter for the Removal of Hydrogen Sulphide Odour. *Int J Environ Res*. 3: 537-544.

[12] Dutta, P. K., Rabaey, K., Yuan, Z., Rozendal, R. A. R. A. Keller, J. J. 2010. Electrochemical Sulfide Removal and Recovery from Paper Mill Anaerobic Treatment Effluent. *Water Res*. 44: 2563-2571.

[13] Sakanishi, K., Wu, Z., Matsumura, A., Saito, I., Hanaoka, T., Minowa, T. 2005. Simultaneous Removal of H_2S and COS using Activated Carbons and Their Supported Catalysts. *Catal Today*. 104: 94-100.

[14] Lemos, B. R. S. S., Teixeira, I. F., de Mesquita, J. P. J. P., Ribeiro, R. R., Donnici, C. L., Lago, R. M. 2012. Use of Modified Activated Carbon for the Oxidation of Aqueous Sulfide. *Carbon*. 50: 1386-1393.

[15] Kazmierczak-Razna, J., Gralak-Podemska, B., Nowicki, P. and Pietrzak, R. 2015. The Use of Microwave Radiation for Obtaining Activated Carbons from Sawdust and Their Potential Application in Removal of NO_2 and H_2S. *Chemical Engineering Journal*. 269: 352-358.

[16] Foo, 5. 5. K. and Hameed, B. H. 2010. Insights into the Modeling of Adsorption Isotherm Systems. *Chemical Engineering Journal*. 156: 2-10.

[17] Sanghi, R., Bhattacharya, B. 2002. Review on Decolorisation of Aqueous Dye Solutions by Low Cost Adsorbents. *Color Technol.* 118: 256-269.

[18] Meshko, V., Markovska, L., Mincheva, M., Rodrigues, A. E. 2001. Adsorption of Basic Dyes on Granular Activated Carbon and Natural Zeolite. *Water Res.* 35: 3357-3366.

[19] Weber, W. J., Morris, J. C. 1964. Hydrophobic Surfaces. Pergamon Press, New York.

[20] Subramaniam, R., Kumar Ponnusamy, S. 2015. Novel Adsorbent from Agricultural Waste (Cashew NUT Shell) for Methylene Blue Dye Removal: Optimization by Response Surface Methodology. *Water Resour Ind.* 11: 64-70.

[21] Zhou, L. 2006. Adsorption: Progress in Fundamental and Application Research: *Selected Reports at the 4th Pacific Basin Conference on Adsorption Science and Technology: Tianjin, China*. 22-26.

[22] Sigot, L., Ducom, G. and Germain, P. 2016. Adsorption of Hydrogen Sulfide (H_2S) on Zeolite (Z): Retention Mechanism. *Chemical Engineering Journal.* 287: 47-53.

[23] Belmabkhout, Y., De Weireld, G., Sayari, A. 2009. Amine-bearing Mesoporous Silica for CO_2 and H_2S Removal from Natural Gas and Biogas. *Langmuir.* 25: 13275-13278.

[24] Bae, J. W., Kang, S-H, Dhar, G. M., Jun, K-W. 2009. Effect of Al_2O_3 Content on the Adsorptive Properties of $Cu/ZnO/Al_2O_3$ for Removal of Odorant Sulfur Compounds. *Int J Hydrogen Energy.* 34: 8733-8740.

[25] Habeeb, O. A., Ramesh, K., Ali, G. A. M., Yunus, R. M. 2017. Isothermal Modelling Based Experimental Study of Dissolved Hydrogen Sulfide Adsorption From Waste Water Using Eggshell Based Activated Carbon. *Malaysian J Anal Sci.* 21: 334-345.

[26] Dabrowski, A., Podkościelny, P., Hubicki, Z., Barczak, M. 2005. Adsorption of Phenolic Compounds by Activated Carbon--A Critical Review. *Chemosphere.* 58: 1049-1070.

[27] Ahmed, S., Rasul, M., Martens, W. 2010. Heterogeneous Photocatalytic Degradation of Phenols in Wastewater: A Review on Current Status and Developments. *Desalination.* 261: 3-18.

[28] Haddadian, Z., Shavandi, M. A., Zainal, Z., Halim, M., Ismail, S. 2013. Removal Methyl Orange from Aqueous Solutions Using Dragon Fruit (Hylocereusundatus) Foliage. *Chem Sci Trans.* 2: 900-910.

[29] Phooratsamee, W., Hussaro, K., Teekasap, S. and Hirunlabh, J. 2014. Increasing Adsorption of Activated Carbon from Palm Oil Shell for Adsorb H_2S from biogas Production by I(mpregnation. *American Journal of Environmental Sciences.* 10: 431-445.

[30] Shang, G., Li, Q., Liu, L., Chen, P. and Huang, X. 2016. Adsorption of Hydrogen Sulfide by Biochars Derived from Pyrolysis of Different Agricultural/Forestry Wastes. J*ournal of the Air & Waste Management Association.* 66: 8-16.

[31] Foo, K. Y., Hameed, B. H. 2011. Microwave Assisted Preparation of Activated Carbon from Pomelo Skin for the Removal of Anionic and Cationic Dyes. *Chem Eng J.* 173: 385-390.

[32] Nowicki, P., Skibiszewska, P., Pietrzak, R. 2013. NO_2 Removal on Adsorbents Prepared from Coffee Industry Waste Materials. *Adsorpt Int Adsorpt Soc.* 19: 521-528.

[33] Misnon, I. I., Zain, N. K. M., Aziz, R. A., Vidyadharan, B. and Jose, R. 2015. Electrochemical Properties of Carbon from Oil Palm Kernel Shell for High Performance Supercapacitors. *Electrochimica Acta.*174: 78-86.

[34] Sumathi, S., Chai, S. P. and Mohamed, A. R. 2008. Utilization of Oil Palm as a Source of Renewable Energy in Malaysia. *Renewable and Sustainable Energy Reviews.* 12: 2404-2421.

[35] Box, G. E. P., Wilson, K. B. 1951. On the Experimental Attainment of Optimum Conditions. J *R Stat Soc Ser B.* 13: 1-45.

[36] Hounsa, C. G., Aubry, J. M., Dubourguier, H. C., Hornez, J. P. 1996. Application of Factorial and Doehlert Designs for Optimization of Pectate Lyase Production by a Recombinant Escherichia Coli. *Appl Microbiol Biotechnol.* 45: 764-70.

[37] Habeeb, O. A., Ramesh, K., Ali, G. A. M., Yunus, R. M. 2017. Optimization of Activated Carbon Synthesis Using Response Surface Methodology to Enhance H2S Removal From Refinery Wastewater. *J Chem Engin Indust Biotechnol.* 1: 1-17.

[38] Azargohar, R., Dalai, A. K. 2005. Production of Activated Carbon from Luscar Char: Experimental and Modeling Studies. *Microporous Mesoporous Mater.* 85: 219-25.

[39] Zainudin, N. F., Lee, K. T., Kamaruddin, A. H., Bhatia, S., Mohamed, A. R. 2005. Study of Adsorbent Prepared from Oil Palm Ash (OPA) for Flue Gas Desulfurization. *Sep Purif Technol.* 45: 50-60.

[40] Hassani, A., Alidokht, L., Khataee, A. R., Karaca, S. 2014. Optimization of Comparative Removal of Two Structurally Different Basic Dyes Using Coal as a Low-cost and Available Adsorbent. *J Taiwan Inst Chem Eng.* 45: 1597-1607.

[41] Roy, P., Mondal, N. K., Das, K. 2014. Modeling of the Adsorptive Removal of Arsenic: A Statistical Approach. *J Environ Chem Eng.* 2: 585-597.

[42] Chaudhary, N., Balomajumder, C. 2014. Optimization Study of Adsorption Parameters for Removal of Phenol on Aluminum Impregnated Fly Ash Using Response Surface Methodology. *J Taiwan Inst Chem Eng.* 45: 852-859.

[43] Alam, M. Z., Ameem, E. S., Muyibi, S. A., Kabbashi, N. A. 2009. The Factors Affecting the Performance of Activated Carbon Prepared from Oil Palm Empty Fruit Bunches for Adsorption of Phenol. *Chem Eng J.* 155: 191-198.

[44] Habeeb, O. A., Ramesh, K., Ali, G. A. M., Yunus, R. M., Olalere, O.A. 2016. Modeling and Optimization for H_2S Adsorption From Wastewater Using Coconut Shell Based Activated Carbon. *Australian J Basic Appl Sci.* 10: 136-147.

[45] Basu, J. K., Monal, D., Pinaki, G. 2012. Statistical Optimization for the Prediction of Ibuprofen Adsorption Capacity by Using Microwave Assisted Activated Carbon. *Arch Appl Sci Res.* 4: 1053-60.

[46] Li, S., Han, K., Li, J., Li, M. and Lu, C. 2017. Preparation and Characterization of Super Activated Carbon Produced from Gulfweed by KOH Activation. *Microporous and Mesoporous Materials.* 243: 291-300.

[47] Chowdhury, Z. Z., Zain, S. M., Khan, R. A., Ahmad, A. A., Khalid, K. 2012. Application of response Surface Methodology (RSM) for Optimizing Production Condition for Removal of Pb (II) and Cu (II) onto Kenaf Fiber based Activated Carbon. *Res J Appl Sci Eng Technol.* 4: 458-465.

[48] Habeeb, O. A., Ramesh, K., Ali, G. A. M., Yunus, R. M. 2017. Experimental Design Technique on Removal of Hydrogen Sulfide Using CaO-Eggshells Dispersed onto Palm Kernel Shell Activated Carbon: Experiment, Optimization, Equilibrium and Kinetic Studies. *J Wuhan Univ Technol-Mater Sci Ed.* 32: 305-32.