JCEIB

Open Access; Volume 1 pp. 1-17; March2017

DOI: https://doi.org/10.15282/JCEIB-V1-01.31/3/2017/1.1.1

# OPTIMIZATION OF ACTIVATED CARBON SYNTHESIS USING RESPONSE SURFACE METHODOLOGY TO ENHANCE $H_2S$ REMOVAL FROM REFINERY WASTEWATER

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

[a] Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Gambang, 26300, Kuantan, Malaysia.

[b] Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Gambang, 26300 Kuantan, Malaysia

[c] Chemistry Department, Faculty of Science, Al–Azhar University, Assiut, 71524, Egypt

[d] Al-Azhar Center of Nanoscience and Applications (ACNA), Al–Azhar University, Assiut, 71524, Egypt

* Corresponding author: ramesh@ump.edu.my

Tel.: +60 17 4536758 Fax: +60 9 5492889

## ABSTRACT

The main point of this study is to investigate the optimal conditions for preparation of activated carbon from wood sawdust (ACWSD) for removal of hydrogen sulfide ($H_2S$) from wastewater. The response surface methodology (RSM) was employed to prepare the ACWSD by chemical activation with potassium hydroxide (KOH). The three preparation variables impact of activation temperature (724 – 1000 °C), KOH: precursor (wt%) impregnation ratio (IR) (2:1 – 4:1) and activation time (60 – 120 min) on removal efficiency (RE, %) of $H_2S$ and activated carbon yield (ACY, %) were investigated. The preparation parameters were correlated by developing a quadratic model depend on the central composite design (CCD) to the two responses. The analysis of variance (ANOVA) was identified the most influential variable on each experimental design responses. The results showed that the temperature of 854 °C, chemical impregnation ratio of 2.95 wt% and activation time of 80 min were the optimum conditions for preparation of ACWSD with responses of RE and ACY of 72.88 % and 31.89 %, respectively. It is concluded that the ACWSD was appeared to be a favorable substance for removal of dissolved $H_2S$ from synthetic wastewater.

*Keywords*: Wood Sawdust, Activated Carbon, Response Surface Methodology, Wastewater, Hydrogen Sulfide.

## 1.0 INTRODUCTION

For a long time people were not informed of the size of the antagonistic impacts of their movement on the nature of the environment. Industrial waste dumps, cluttered forests, polluted air and poisoned rivers are the impacts of the actions of human on the environment. The outflow of gasses including to for example carbon oxides, hydrogen sulfide, nitrogen oxides and sulfur dioxide was regarded to the main reason for the phenomena of acid rain, smog pollution, odors as well as for decreasing in the layers of ozone (Kazmierczak-Razna *et al.*, 2015). In addition, the globalization effect has resulted in the emergence and development of different industrial institutions and this

has led to a noticeable upsurge of accrued wastes which has grueling impacts on the environment. Basically, the contemporary community is urgent to improve to gage and handle these wastes for protecting the environment and secure human well-being. For example, in the industry of crude oil processing this can be produced by high and low sulfur contents, respectively. Because of the toxicity of sulfur, the most preferred over its sour counterpart is sweet crude oil (Purcell *et al.*, 2007). In fact, there will be many wastes which would dissolve inevitably in the water especially when the distillate crude oil is processed into useful products to inevitably produce sour water which is hazardous (containing ($H_2S$)) and hence it must be treated before the discharge for reuse or discard to moor.

Moreover, polluted water is lethal to organisms in the bottom as well as causes exhaustion of dissolved oxygen (Kienow, 1989). Furthermore, $H_2S$ causes respiratory issues, safety issue by its very combustible nature and additionally monetary issues emerging from erosion of metals (even in the low level of $H_2S$) (Ozekmekci *et al.*, 2015). Regardless to the corrosion of metal because the $H_2S$, the rigid surface would be also corroded because the steady formation of sulfuric acid and ultimately causes destroy the sewer system (Vollertsen *et al.*, 2008). Besides the corrosion problems caused, $H_2S$ is very toxic and can be observed in an amount between 0.05 and 0.1 mg/L. For mentioned above the significance of taking measurements distillate on the protection of the environment, including those directed to the limitation of emission of pollutants.

An adsorption on the activated carbon is a vital technique that can be created for the expulsion of pollutants from air and water (Bansal & Goyal, 2005). The widespread difference of the fossil carbonaceous substances, for instance, wool, peat and coal can be used as a carbon precursor for activated carbons. Furthermore, the wastes of wood and farming are cheap and recyclable extra sources for activated carbons. It is believed that these wastes substances have less or no costs, and their discarding often becomes the main problem. For instance, in Malaysia, every year there is almost million tons of farming wastes are being discarded into landfills (Hameed *et al.*, 2007). In this manner, the value added process can be obtained through the transformation of waste substances into activated carbon. Similarly, the burden of waste disposal can be decreased as well as provides a possible cheap shifted material to the current commercial activated carbons (Tsai *et al*., 2007). Lastly, many researchers have been conducted on activated carbon from agricultural wastes, such as sugar canes (Castro *et al.*, 2000; Rufford *et al.* 2010), nut shell (Hu & Vansant, 1995), coconut shell (Yang *et al*., 2010), fruit stones (Lussier *et al*., 1994; Kazemipour *et al.* 2008), macadamia nut shells (Martins *et al.*, 2015), fibers of oil palm empty fruit bunches (Farma *et al.*, 2013), sunflower straw (Foo & Hameed, 2011b) and date stones (Sekirifa *et al.*, 2013).

Activated carbon has large adsorption capacity due to it has a great permeability and large-surface-area materials which is created by activation of carbonaceous substances and carbonization. They are widely utilized as catalyst supports and electrode materials of supercapacitors and also for purification and filtration applications. Moreover, since their large surface area and permeability, the existence of different practical groups permits a broad application of activated carbons like pesticide adsorption to decrease pollutant and nutrient preservation in soil (Rajkovich *et al.*, 2012). It is possible to use jacaranda fruit and plum kernels to produce activate carbons which are used in water

treatment (Treviño-Cordero *et al*., 2013). A great deal of attention has been paid to the preparation and characterization of activated carbons in both industrial and scientific field. This attention is because of a large number of applications. The activated carbon which is produced by the chemical activation has a higher surface area and a higher yield at a lower temperature compared with that activated carbons produced by physical activation (Demirbas, 2009). As a consequence of the degree of surface area development, there is a high flexibility in the sorption, kind of permeable construction and particular character of its surface (Nowicki *et al*., 2013; Adib *et al*., 1999). The properties and efficiency of activated carbons give them precious value particularly in industrial conditions for refining of water (Foo & Hameed, 2011a), gases (Pietrzak & Bandosz, 2007; Bansode *et al*., 2003), wastewater (Wang *et al*., 2008) as well as catalysts supports (Santoro *et al*., 2003). Very few studies reported on the removal of $H_2S$ from aqueous solution using activated carbon (AC) under applying the application response surface method (RSM).

In this study, RSM technique is used to optimize the preparation of activated carbon for the removal of $H_2S$ from synthetic wastewater. RSM is a useful statistical model tool and it can be utilized to assess the relative importance of several influencing elements even in the existence of composite interactions. (Hounsa *et al*., 1996). The objectives of this work are to investigate the optimum adsorbent preparation factors needed to maximize the removal efficiency of $H_2S$ from wastewater.

## 2.0 METHODS AND MATERIALS

### Raw Materials

Wood sawdust was a source of carbon. It was collected from a sawmill in Kuantan, Malaysia. The sawdust was filtered to vacate any impurities, dehydrate at 110 °C for 24 h and stored in a sealed container. Later, the dried wood sawdust was milled utilizing a lab-scale milling machine speed of around 500 rpm and grinded to volume of 0.5 – 1 mm. Then, the result wood sawdust was activated with KOH: wood sawdust (IR) bulk proportions of 2:1 – 4:1 using Equation 1:

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

Where, IR is the impregnation ratio, $W_{KOH}$ is the weight (g) of KOH pallets and $W_c$ is the weight (g) of wood saw dust.

### Activated Carbons Preparation

The activation process of wood sawdust was implemented based on the suggestion of software. The activation process was conducted by using a horizontal tubular furnace (Nabertherm, R5/500, Germany). The samples were subjected to a pyrolysis process under conditions were shown in Table 1. The heating rate was 10 °C/min in an inert atmosphere ($N_2$ flow of 150 mL/min) for the production of activated carbon. The last products are washed and dehydrated at 110 °C for 24 h and coded as ACWSD. All the chemical used are gotten from faculty of chemical engineering and natural resources laboratory store University Malaysia Pahang.

**Hydrogen Sulfide Solution Preparation**

In this study, the artificial waste water of the hydrogen sulfide solution was prepared according to the procedure used by Asaoka (Asaoka *et al*., 2009). Then, the pH of the mixture is adjusted to neutral utilizing 0.2 M HCl.

**Modelling and Optimization**

***Experiment design***

Response surface methodology (RSM) is an accumulation of numerical and statistical methods that are important for illustrating, examination, demonstrating and investigation of problems in which a response of interest effected by a couple factors (Montgomery, 2001). Central composite design (CCD), three-level factorial design and Box–Behnken design are considered the several classes of designs under RSM and they are the most common designs utilized by the scholars. However, in the current study the CCD was employed to study optimization and the effect of factors toward their responses. This method is suitable for fitting a quadratic surface and it spreads to enhance the influential parameters with a minimum number of experiments as well as examine the association between the parameters (Montgomery, 2001). With a specific end goal to figure out whether the elements and the response variables explored can be associated and using a regression as an appropriate method to analyze the information gathered.

Commonly, the CCD comprises of a 2k axial or star runs with 2k factorial runs and centre runs nc (Azargohar & Dalai, 2005). The three parameters investigated were the temperatures activation (T), mass ratio of KOH : precursor and the duration of time activation (t) and their related extends were 724 – 1000 °C, 2:1 – 4:1 and 60 – 120 min, respectively. The responses were RE and ACY. At the centre point were performed six replications. Thus, the whole number of experiment (N) needed is as follows:

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

The residual error was estimated by replicating the central point. Based on the extend of each element (factor), the independent factors are coded to the (-1,1) interval. The different levels, that is to say, high and low, are coded +1 and -1 separately. The axial points are situated at (0,0,±œ), (±œ,0,0), (0,±œ,0), what makes the design rotatable is the œ which represents the axial point from the centre. The value of œ is 1.565 as suggested by software. For designing this set of the experiment the design of expert software version 10 was utilized. In the recent study, the conditions of preparation elements for prepared activated carbon based wood sawdust (ACWSD) by utilizing the CCD. The variables studied were (i) $x_1$, activation temperature (°C); (ii) $x_2$, KOH: precursor mass ratio and (iii) $x_3$, activation time. The outcomes acquired and complete design matrix of the tests did, all together, are appeared in Table 1. The purpose behind of randomizing the experimental result was to diminish the effect of the uncontrolled constituents. The removal efficiency RE was considered as a response and AC yield. In order to set up an empirical model the responses were used which in turn correlate the responses to three preparation elements using a second degree polynomial equation as given by Equation 3 (Zainudin *et al.*, 2005):

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (3)$$

where *Y* is the predicted response, *bo* 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.

***Model fitting and statistical analysis***

Design-Expert software (version DX10) was conducted to determine the regression and graphical analysis with statistical significance. In order to picture the relationship between the responses and experimental factors, the contour plots and response surface were created from the models. The best values of the process s variables were obtained from the reaction surface. A coefficient of determination (*R*-squared), Fisher value (*F*-value), probability (*P* value), and residual were used as a standard of significance of the model equations (Hassani *et al.*, 2014; Roy *et al.*, 2014). Graphs were utilized to investigate the combined impact of variables on responses utilizing 3D plots and to also analyze the actual value versus the predicted plots of the response variables.

***Optimization and validation***

Optimization strategy was utilized to decide the optimum preparation conditions for the procedure factors under consideration. To accomplish this, objectives were set with requirements. For each of the variables, goal was set "in range" with limitations 724 – 1000 °C, 2:1 – 4:1 and 60 – 120 min of lower-upper level for factors activation temperatures, mass ratio of KOH: precursor and time duration of activation (t), respectively. For the responses surface, the objective for RE and ACY were set "maximize". Subsequently adsorption capacity becomes the objective function or performance index. Furthermore, the three validations runs were conducted via carrying out batch experiment under optimal preparation conditions. To assess the model validation, the experimental values obtained were matched to the model predicted values.

**Batch Equilibrium Studies**

Batch adsorption was implemented to conduct the adsorption of $H_2S$ onto ACWSD and its capability for removal of $H_2S$ from wastewater. The experimental work was conducted in 34 sets of 250 mL Erlenmeyer vials. The amount of 100 mL of $H_2S$ solution with initial $H_2S$ concentration of 500 mg/L was placed in each vial. The pH of the solution was adjusted to neutral. A 0.1 g of each of the prepared activated carbon was added to each vial and kept in a thermostated shaker of 150 rpm at 30 °C until equilibrium was reached. Aqueous samples were taken from the solutions and the concentrations were analyzed by spectrophotometer HACH DR2800 using sulfide reagent 1&2 (Method: Methylene Blue). The Equation 4 was used to determine $q_e$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

where V is the solution (L) volume, m is the adsorbent (g) amount, $C_o$ and $C_e$ are the initial and final concentrations in the pollutants, and ($q_e$) is adsorption capacity $mg.g^{-1}$,

$m$ = mass of activated carbon used (g). The sample yield was calculated using Equation 5:

$$Yield(\%) = \frac{W_C}{W_\circ} \times 100\% \quad (5)$$

where Wc and W◦ are the dry weight of product (g) and the dry weight of precursor (g)

$$Removal\ effeciency = \frac{C_0 - C_e}{C_0} X100 \quad (6)$$

## 3.0 RESULTS AND DISCUSSIONS

### 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 °C), activation mass ratio KOH: precursor (2:1 – 4:1 w %) (Shaaban *et al.*, 2015), and activation time (60 – 120 min) were deemed as the independent operation elements and their interactive and individual impacts on the $H_2S$ removal Efficiency RE and ACY (as responses) were examined utilizing the approach of CCD. The quadratic polynomial model was chosen for the developing the mathematical rapport between the responses and the preparation process factors. The predicted and experimental values for both responses (RE and ACY) and coded, uncoded preparation factors corresponding to different combinations of selected factors are showed in Table 1.

In addition, Correlation between the factors and responses surface were improved utilizing CCD of the software of design expert. Based on the sum of the successive model the selection of models relied on the highest order polynomials where the additional terms were the model were not significant and identified (Chaudhary & Balomajumder, 2014). Correlation coefficient and standard deviation were used to obviate the model developed fitness. The better the model in forecasting the response is the smaller the standard deviation and the closer the $R^2$ value is to unity (Alam *et al.*, 2009).

**Table 1:** The 3 factors central composite design matrix and the values of the responses function.

| Runs | ACWSD preparation conditions variables | | | | | | RE (%) | ACY (%) |
|---|---|---|---|---|---|---|---|---|
| | Coded variables | | | A: Activation temperature (°C) | B: KOH: precursor ratio | C: Activation time (min) | | |
| 1 | 1.000 | 1.000 | -1.000 | 1000.00 | 4.00 | 60.00 | 70 | 25 |
| 2 | 0.000 | 0.000 | -1.565 | 862.00 | 3.00 | 43.05 | 70.5 | 32.4 |
| 3 | 1.000 | -1.000 | -1.000 | 1000.00 | 2.00 | 60.00 | 69.6 | 26 |
| 4 | 1.565 | 0.000 | 0.000 | 1077.98 | 3.00 | 90.00 | 67.5 | 19.5 |
| 5 | -1.000 | 1.000 | -1.000 | 724.00 | 4.00 | 60.00 | 67.7 | 28.5 |
| 6 | 1.000 | -1.000 | 1.000 | 1000.00 | 2.00 | 120.00 | 67.2 | 24.5 |
| 7 | -1.000 | 1.000 | -1.000 | 724.00 | 4.00 | 60.00 | 67.9 | 28.2 |
| 8 | 1.000 | 1.000 | 1.000 | 1000.00 | 4.00 | 120.00 | 67.2 | 23 |
| 9 | 0.000 | 1.565 | 0.000 | 862.00 | 4.57 | 90.00 | 68.43 | 28 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 10 | 0.000 | 1.565 | 0.000 | 862.00 | 4.57 | 90.00 | 68.5 | 28 |
| 11 | 0.000 | -1.565 | 0.000 | 862.00 | 1.43 | 90.00 | 68 | 30 |
| 12 | 0.000 | 0.000 | 1.565 | 862.00 | 3.00 | 136.95 | 69.5 | 30 |
| 13 | 1.565 | 0.000 | 0.000 | 1077.98 | 3.00 | 90.00 | 67.5 | 19.5 |
| 14 | -1.000 | -1.000 | 1.000 | 724.00 | 2.00 | 120.00 | 68.5 | 28.5 |
| 15 | -1.000 | -1.000 | -1.000 | 724.00 | 2.00 | 60.00 | 66.9 | 30.4 |
| 16 | -1.000 | 1.000 | 1.000 | 724.00 | 4.00 | 120.00 | 68.12 | 28 |
| 17 | -1.000 | -1.000 | -1.000 | 724.00 | 2.00 | 60.00 | 67 | 31 |
| 18 | 0.000 | 0.000 | 1.565 | 862.00 | 3.00 | 136.95 | 69.5 | 30 |
| 19 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 72.8 | 31.6 |
| 20 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 73 | 31 |
| 21 | -1.000 | -1.000 | 1.000 | 724.00 | 2.00 | 120.00 | 68 | 28.7 |
| 22 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 73 | 31.9 |
| 23 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 73 | 31.7 |
| 24 | 1.000 | 1.000 | 1.000 | 1000.00 | 4.00 | 120.00 | 67 | 23.3 |
| 25 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 73 | 31.5 |
| 26 | -1.000 | 1.000 | 1.000 | 724.00 | 4.00 | 120.00 | 68 | 27.7 |
| 27 | 1.000 | -1.000 | -1.000 | 1000.00 | 2.00 | 60.00 | 70 | 26.3 |
| 28 | 0.000 | 0.000 | 0.000 | 862.00 | 3.00 | 90.00 | 73.5 | 31 |
| 29 | 1.000 | 1.000 | -1.000 | 1000.00 | 4.00 | 60.00 | 70.3 | 24.8 |
| 30 | -1.565 | 0.000 | 0.000 | 646.02 | 3.00 | 90.00 | 66.5 | 27 |
| 31 | 1.000 | -1.000 | 1.000 | 1000.00 | 2.00 | 120.00 | 67 | 25.3 |
| 32 | -1.565 | 0.000 | 0.000 | 646.02 | 3.00 | 90.00 | 66.9 | 27 |
| 33 | 0.000 | -1.565 | 0.000 | 862.00 | 1.43 | 90.00 | 68.2 | 30.5 |
| 34 | 0.000 | 0.000 | -1.565 | 862.00 | 3.00 | 43.05 | 70.5 | 32.7 |

**The Equation of Regression Model**

The software of design expert was utilizing through CCD in order to develop the correlation between the factors and response surface. Regarding assess the wellness of the development of models, standard deviation and relationship coefficient were used. As showed by sequential model combined of squares, the model was selected in the light of the most amazing demand polynomials where the extra periods were remarkable and models were not linked (Chaudhary & Balomajumder, 2014; Tan *et al*., 2008). The $R^2$ values of 0.975 and 0.9901 estimated that 97.5% and 99.01 % of the difference in RE and ACY could be attributed to the three factors (A- activation temperature, B- KOH: precursor ratio, C- activation time. Therefore, the quadratic model suggested by the software can be written as:

$$RE = 72.91+0.34A+0.12B-0.45C-0.039AB-0.91AC-0.17BC-2.22A^2-1.74B^2-1.04C^2 \quad (7)$$

$$ACY=31.50-2.18A-0.75B-0.74C+0.012AB-0.050AC+0.14BC-3.42A^2-1.02B^2-0.15C^2 \quad (8)$$

**3.3 Statistical Analysis**

The analysis of variance (ANOVA) and lack of fit test for response surface quadratic model for RE are shown in Table 2. It is possible to notice from the Table 2 that the F-value of the quadratic model is (103.97). The model is significance since the p value is less than (0.05) (Basu *et al.*, 2012). Consequently, the terms of the significant model are

A, C, $A^2$, $B^2$, $C^2$ and AC, while AB, B and BC are the insignificant model terms. While Table 3 represented the analysis of variance (ANOVA) and lack of fit test for response surface quadratic model for ACY which shows that the quadratic model is significant due to it has the F-value of 265.83, and P-value less than 0.0001 (Basu *et al.*, 2012). Therefore, the significant model terms are A, B, C, $A^2$, and $B^2$, while AB, AC, BC and $C^2$ are the insignificant model terms. The lack of fit compares the residual error to the pure error from replicated design points. Thus, the centre point result is very close to each other which lead to effect the lack of fit of model. So the lack of fit was significant for both models.

**Table 2:** 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 | 149.56 | 9 | 16.62 | 103.97 | < 0.0001 | significant |
| A-Activation temperature | 2.92 | 1 | 2.92 | 18.29 | 0.0003 | significant |
| B-KOH: precursor ratio | 0.39 | 1 | 0.39 | 2.43 | 0.1325 | insignificant |
| C-Activation time | 5.14 | 1 | 5.14 | 32.13 | < 0.0001 | significant |
| AB | 0.024 | 1 | 0.024 | 0.15 | 0.7016 | insignificant |
| AC | 13.36 | 1 | 13.36 | 83.58 | < 0.0001 | significant |
| BC | 0.48 | 1 | 0.48 | 3.02 | 0.0949 | insignificant |
| $A^2$ | 93.13 | 1 | 93.13 | 582.66 | < 0.0001 | significant |
| $B^2$ | 57.02 | 1 | 57.02 | 356.74 | < 0.0001 | significant |
| $C^2$ | 20.27 | 1 | 20.27 | 126.81 | < 0.0001 | significant |
| Residual | 3.84 | 24 | 0.16 | | | |
| Lack of fit | 3.14 | 5 | 0.63 | 17.03 | < 0.0001 | significant |

**Table 3:** Analysis of variance (ANOVA) and lack of fit test for response surface quadratic model for adsorbent ACY.

| Sources | Sum of squares | df | Mean square | F-value | P-value | Comment |
|---|---|---|---|---|---|---|
| Model | 383.10 | 9 | 42.57 | 265.83 | <0.0001 | significant |
| A-Activation temperature | 122.76 | 1 | 122.76 | 766.65 | <0.0001 | significant |
| B-KOH: precursor ratio | 14.35 | 1 | 14.35 | 89.64 | <0.0001 | significant |
| C-Activation time | 14.26 | 1 | 14.26 | 89.07 | <0.0001 | significant |
| AB | 2.500E-003 | 1 | 2.500E-003 | 0.016 | 0.9016 | insignificant |
| AC | 0.040 | 1 | 0.040 | 0.25 | 0.6218 | insignificant |
| BC | 0.30 | 1 | 0.30 | 1.89 | 0.1820 | insignificant |
| $A^2$ | 221.46 | 1 | 221.46 | 1383.03 | <0.0001 | significant |
| $B^2$ | 19.82 | 1 | 19.82 | 123.78 | <0.0001 | significant |
| $C^2$ | 0.40 | 1 | 0.40 | 2.52 | 0.1255 | insignificant |
| Residual | 3.84 | 24 | 0.16 | | | |
| Lack of fit | 2.26 | 5 | 0.45 | 5.41 | 0.0029 | significant |

Figure 1a and 1b demonstrates the plots of actual versus predicted values of response RE and ACY values which shows the experimental values are quite close to the predicted values, showing that the model developed is successful indicating that these

response surface model equations could be utilized to adequately shows the interaction of the three factors.

Table 4 demonstrates the regression statistics for quadratic model for RE response which has generally small standard deviation of 0.40 and moderately high $R^2$ value of 0.9759 with predicted $R^2$ (0.9484) in reasonable agreement with adjusted $R^2$ (0.9656). 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 5 likewise demonstrates the regression statistics for quadratic model for ACY which has a moderately small standard deviation of 0.40 and generally high $R^2$ value of 0.9901 with predicted $R^2$ (0.9793) in reasonable agreement with adjusted $R^2$ (0.9863) and the quadratic model for response $R^2$ was not aliased. This implies that the quadratic model can be employed to describe the relationship between the interacting factors and responses. The predicted $R^2$ is represented the fitted of the predicted values by the software.

**Table 4:** Regression statistics for removal efficiency RE at equilibrium.

| Source | Standard deviation | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | Comment |
|---|---|---|---|---|---|
| Linear | 2.20 | 0.0551 | -0.0394 | -0.0985 | |
| 2FI | 2.20 | 0.1455 | -0.0444 | -0.0648 | |
| Quadratic | 0.40 | 0.9750 | 0.9656 | 0.9484 | Suggested |
| Cubic | 0.41 | 0.9781 | 0.9639 | 0.9299 | Aliased |

**Table 5:** Regression statistics for adsorbent ACY at equilibrium.

| Source | Standard deviation | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | Comment |
|---|---|---|---|---|---|
| Linear | 2.80 | 0.3912 | 0.3303 | 0.2466 | |
| 2FI | 2.95 | 0.3921 | 0.2570 | 0.1915 | |
| Quadratic | 0.40 | 0.9901 | 0.9863 | 0.9793 | Suggested |
| Cubic | 0.31 | 0.9950 | 0.9918 | 0.9862 | Aliased |

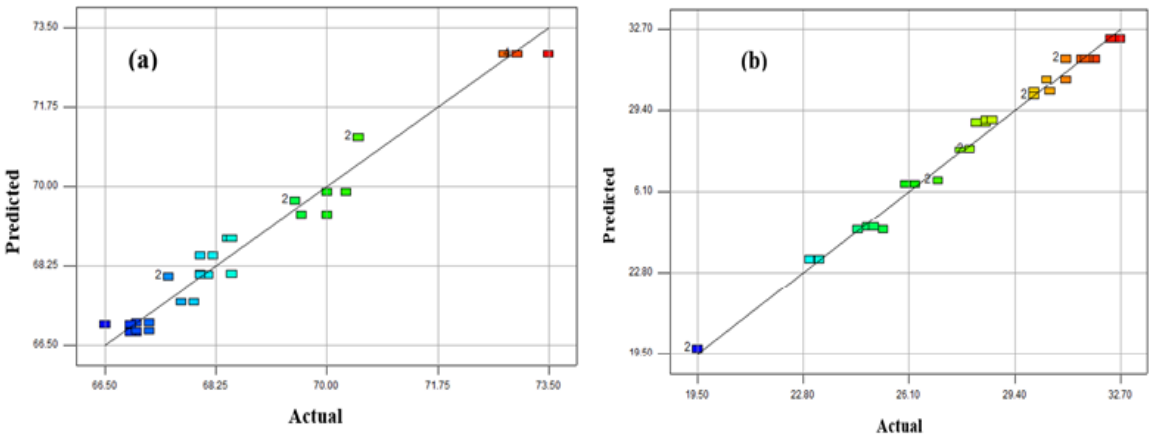


**Figure 1**. Actual and predicted curve for (a) RE and (b) ACY.

**Combined effect of factors on response of removal efficiency.**

The 3D response surfaces of the combined effect of activation temperature and KOH: precursor ratio at constant of activation time on response RE is shown in Figure 2. It shows the clear interactions between these two parameters. The activation temperature with a range between 724 to 1000 °C and mass ratio of (KOH: precursor) with range of (2:1 - 4:1 w%). So from 3D graphs which shows in Figure 2. It could be clearly noticed that the effect of activation temperature and activation mass ration have significant impact on the RE value. At the low activation temperature around 724 °C, the value of RE % was very low which around 67%. 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 854 °C with RE of 72.88 %. Moreover, the activation agent also has important effect on the response RE. As could be seen from Figure 2. as low KOH : precursor as low the RE then the percentage of RE increased when KOH: precursor increased that mean the chemical activation attributed more on the RE same trend observed on previous work (Chowdhury *et al.*, 2012)

Figure 3 shows the 3D response surfaces of the combined effect of activation time and activation temperature of AC at constant KOH: precursor on the response of RE. The combined effect of activation time range (60 - 120 min) and activation temperature on AC range (724 - 1000 °C) have a significant effect on response RE. From Figure 3 at the lower values of factors, it is observed that both factors have low impact on the RE % process at the beginning. However, the effect of factors increased with increasing activated temperature and activation time until reach the optimum activation time and temperature that required to improve the RE which is around 79.5 (min) and 854 °C respectively. Moreover, activation temperature has higher impact on the response RE % compared with activation time (Figure 3).

Figure 4 shows the three-dimensional response surfaces of the combined effect of activation time and KOH: precursor at constant of activation temperature of AC on response RE. From Figure 4 it could be seen that activation time has relatively comparable effect with KOH: precursor on response RE. However, the KOH: precursor has more impact on the RE as seen in Figure 4. It can be seen from Figure 4 that activation time has very low RE at (120 min) which is the higher activation time value.

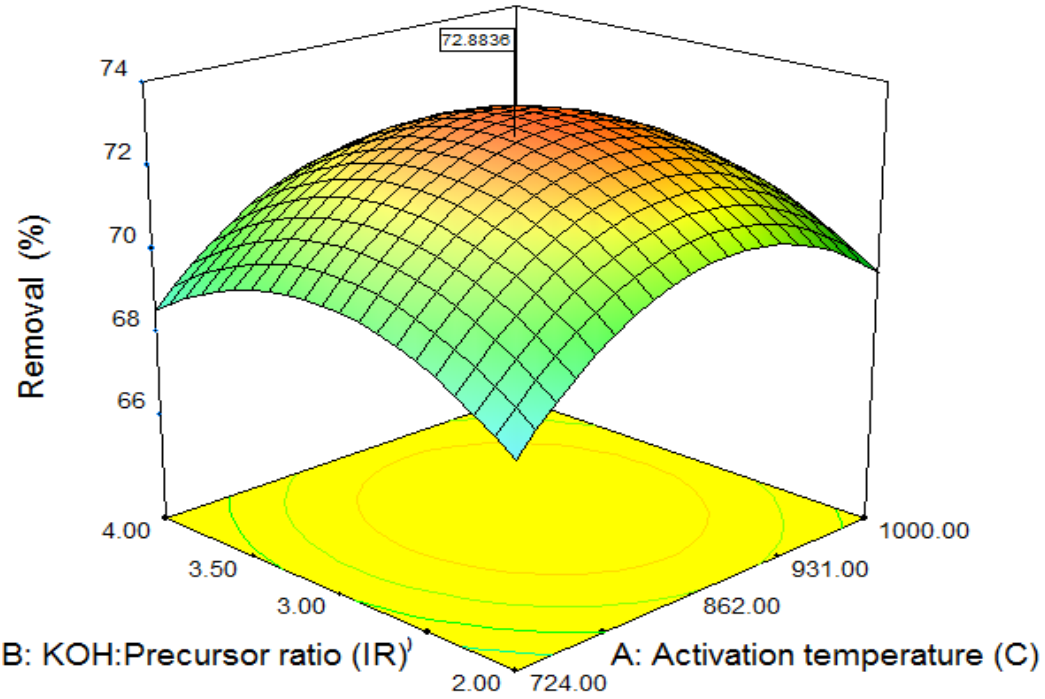


**Figure 2:** Combined impact of activation temperature and KOH: precursor ratio at constant of activation time on response RE.

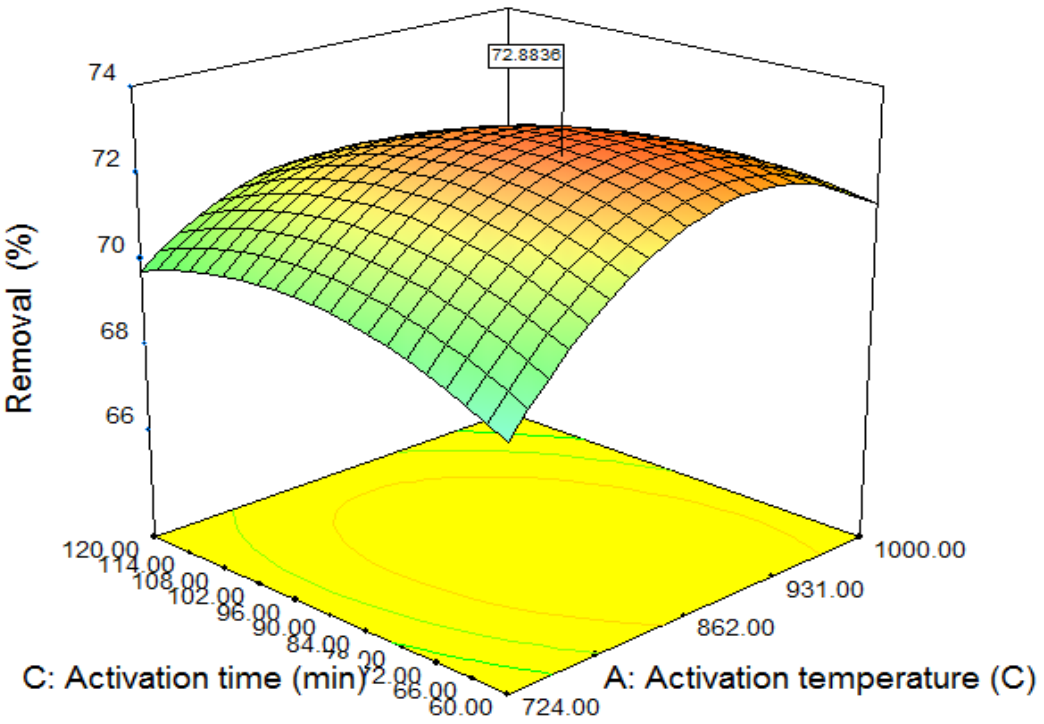


**Figure 3:** Combined impact of activation time and activation temperature of AC at constant KOH: precursor ratio on the response of RE.

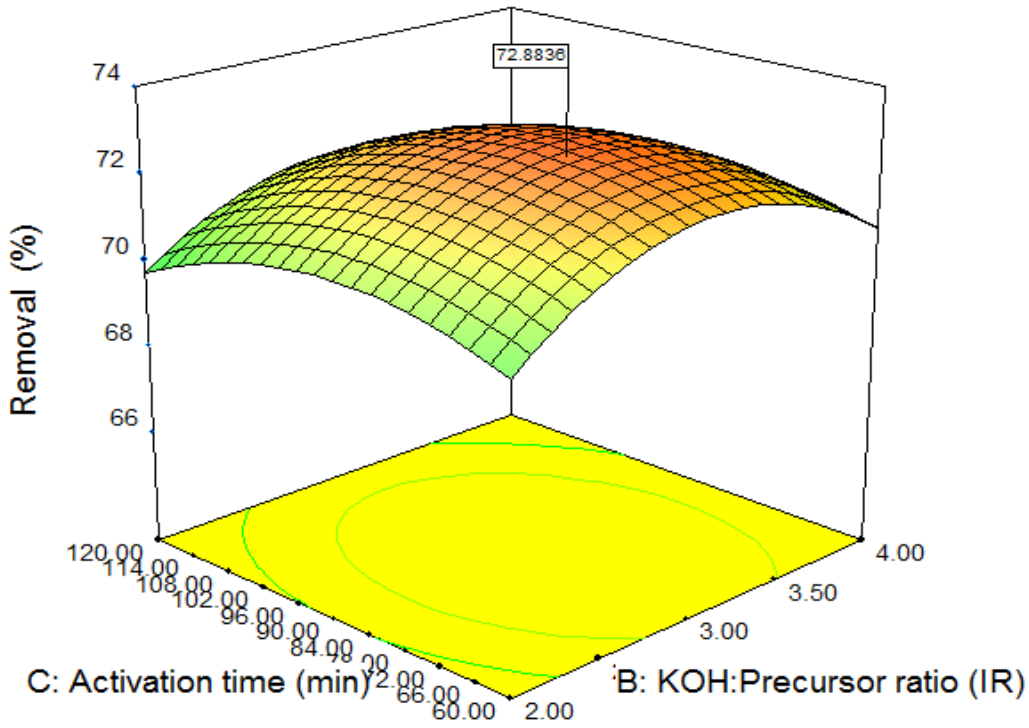


**Figure 4:** Combined impact of activation time and KOH: precursor ratio at constant of activation temperature of AC on response RE.

**Combined Effect of Factors on Response of Activated Carbon Yield**

Figure 5 demonstrates the combined effect of KOH: precursor ratio and activation temperature of AC on ACY at constant of activation time. It could be seen from the 3D graph that the factor of activation temperature on AC has the most impact on the response AC yield % compared with the KOH: precursor ratio factors. The product of AC yield decreased when the activation temperature increased. While the effect of factor of KOH: precursor ratio was quite smaller as increased of KOH: precursor the yield decreasing (Figure 5).

Figure 6 demonstrated the 3D response surfaces of the combined effect of activation time and activation temperature of AC on ACY at constant KOH: precursor ratio. From Figure 6 it is noticed that the effect of activation temperature of AC has a huge impact on yield. It could be clearly observed the increasing the activation time and temperature leads to decrease ACY. On the other hand, the effect of activation time is relatively low during the process as the activation time value decreased the yield start increased until reach the optimum activation time required to get optimum yield which is around 52 min.

Figure 7 shows the three-dimensional response surfaces of the combined effect of activation time and KOH: precursor ratio on ACY at constant activation temperature of AC. From Figure 7 it shows that the activation time has an almost significant effect on ACY. It could be seen that activation time has a very low yield at (120 min) which is the higher activation time value. Thus, the ACY increased when the activation time decreasing until reach the optimum values of the ACY.

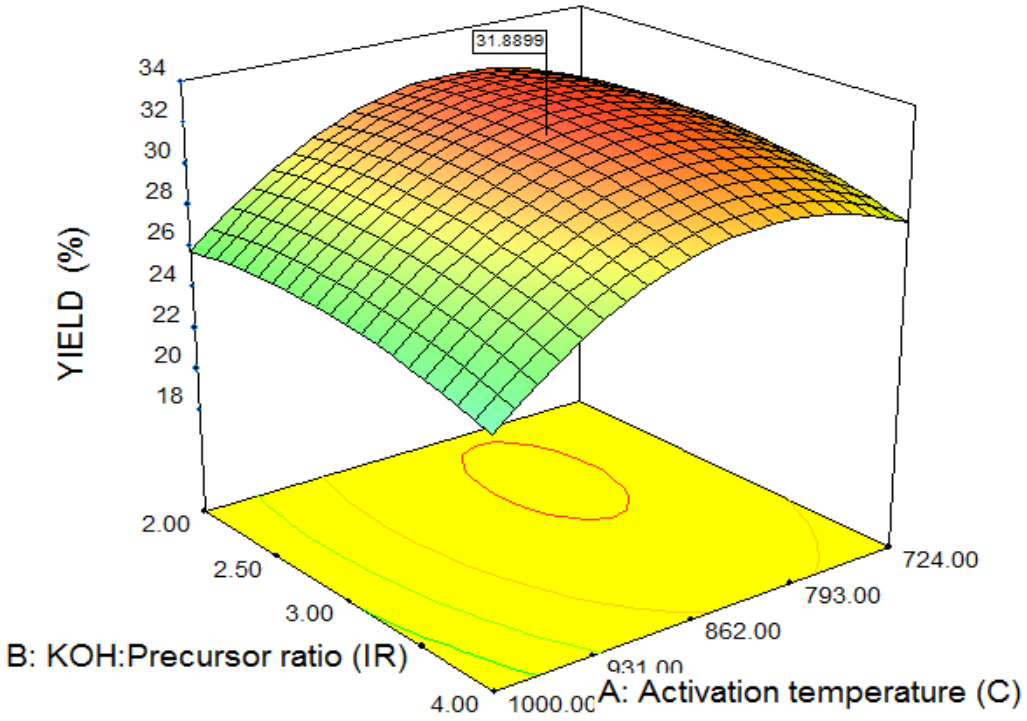


**Figure 5:** Combined impact of KOH: precursor ratio and activation temperature of ACY at constant of activation time.

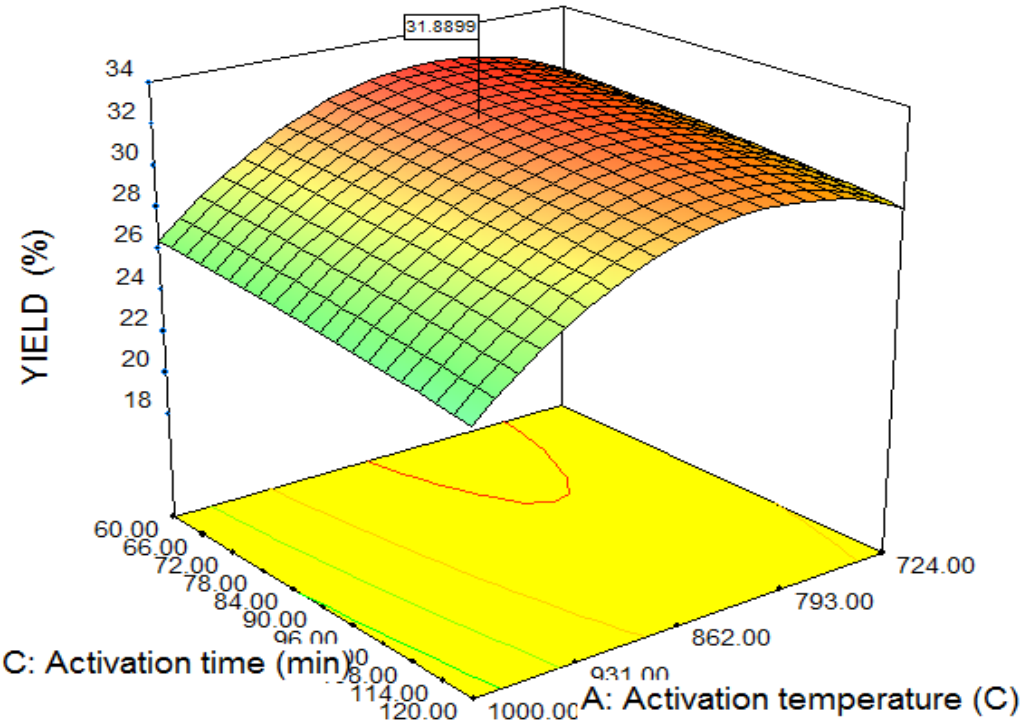


**Figure 6:** Combined impact of activation time and activation temperature of ACY at constant KOH: precursor ratio.

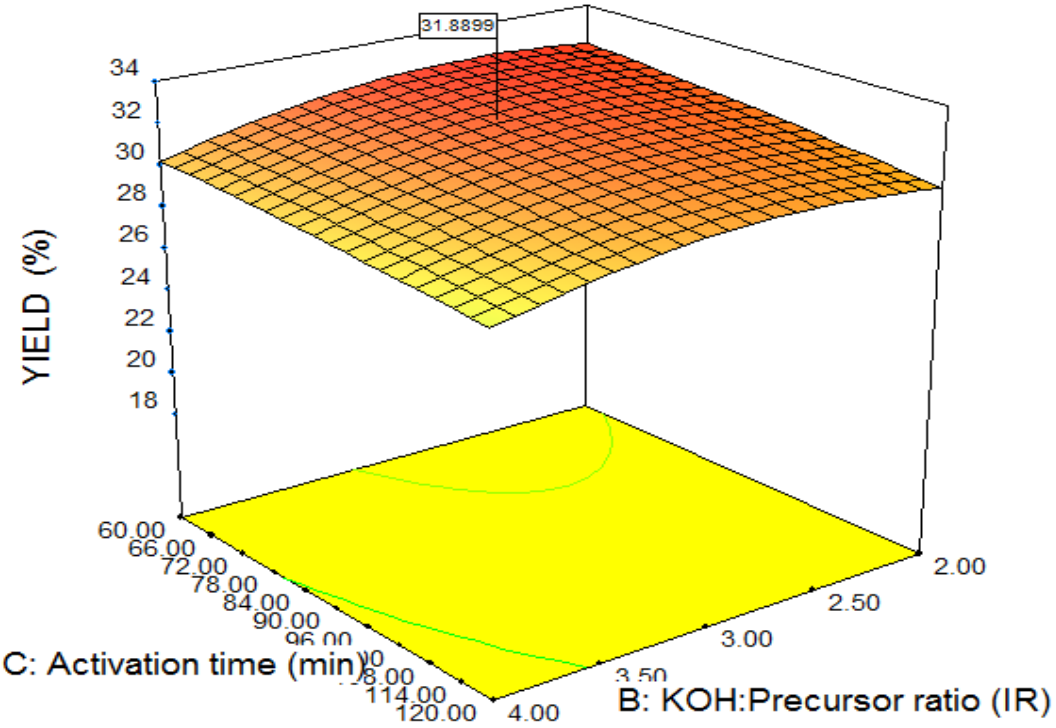


**Figure 7:** Combined impact of activation time and KOH: precursor ratio on ACY at constant activation temperature.

**Model Validation**

The preparation AC factors optimum condition are: *A*- activation temperature of AC = 854 °C, *B*- KOH: precursor = 2.95 w%, and C- activation time = 80 minutes. The result is tabulated in Table 6. It is found that the means of experimental RE and ACY values after repeating three times compares well with the RSM model predicted values. The percentage error is low (4.3 - 4.6) %, therefore, the model equation suggested by RSM is valid and can be used to predict the responses factors of RE and ACY accurately.

**Table 6:** Model validation

| Variables | | | Theoretical | | Experimental | | Percentage error | |
|---|---|---|---|---|---|---|---|---|
| Activation temperature (℃) | KOH : precursor ratio | Activation time (min) | RE (%) | ACY (%) | RE (%) | ACY (%) | RE (%) | ACY (%) |
| 854 | 2.95 | 80 | 72.88 | 31.89 | 69.5 | 30.5 | 4.6 | 4.3 |

## 4.0 CONCLUSIONS

The preparation conditions factors of activated carbon from wood sawdust (ACWSD) for $H_2S$ removal from wastewater was investigated. The adsorbent was produced under optimum removal efficiency and yield. The analysis of variance (ANOVA) was identified the most influential variable on each experimental design responses. The result shows that the temperature of 854 °C, chemical impregnation ratio of 2.95 wt% and activation time of 80 min were the optimum conditions for preparation of ACWSD

with responses of removal efficiency and yield of 72.88 % and 31.89 % respectively. It is concluded that the ACWSD was appeared to be a favorable substance for removal of dissolved $H_2S$ from synthetic wastewater.

## ACKNOWLEDGEMENT

This work was funded by Faculty of Chemical & Natural Resources Engineering, University Malaysia Pahang through a local research grant scheme (ERGS) No.: RDU130618.

## REFERENCES

Adib, F., Bagreev, & Bandosz, T. (1999). Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide. *Journal of Colloid and Interface Science*, *214*(2), 407–415.

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. *Chemical Engineering Journal*, *155*(1), 191–198.

Asaoka, S., Yamamoto, T., Kondo, S., & Hayakawa, S. (2009). Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments. *Bioresource Technology*, *100*(18), 4127–4132.

Azargohar, R., & Dalai, A. K. (2005). Production of activated carbon from Luscar char: experimental and modeling studies. *Microporous and Mesoporous Materials*, *85*(3), 219–225.

Bansal, R. C., & Goyal, M. (2005). *Activated carbon adsorption*, CRC press.

Bansode, R. R., Losso, J. N., Marshall, W. E., Rao, R. M., & Portier, R. J. (2003). Adsorption of volatile organic compounds by pecan shell-and almond shell-based granular activated carbons. *Bioresource Technology*, *90*(2), 175–184.

Basu, J. K., Monal, D., & Pinaki, G. (2012). Statistical optimization for the prediction of ibuprofen adsorption capacity by using microwave assisted activated carbon. *Archives of Applied Science Research*, *4*(2), 1053–1060.

Castro, J. B., Bonelli, P. R., Cerrella, E. G., & Cukierman, A. L. (2000). Phosphoric acid activation of agricultural residues and bagasse from sugar cane: influence of the experimental conditions on adsorption characteristics of activated carbons. *Industrial & Engineering Chemistry Research*, *39*(11), 4166–4172.

Chaudhary, N., & Balomajumder, C. (2014). Optimization study of adsorption parameters for removal of phenol on aluminum impregnated fly ash using response surface methodology. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(3), 852–859.

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. *Research Journal of Applied Sciences, Engineering and Technology*, *4*(5), 458–465.

Demirbas, A. (2009). Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. *Journal of Hazardous Materials*, *167*(1), 1–9.

Farma, R., Deraman, M., Awitdrus, A., Talib, I. A., Taer, E., Basri, N. H., & Hashmi, S. A. (2013). Preparation of highly porous binderless activated carbon electrodes from fibres of oil palm empty fruit bunches for application in supercapacitors.

*Bioresource Technology*, *132*, 254–261.

Foo, K. Y., & Hameed, B. H. (2011a). Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes. *Chemical Engineering Journal*, *173*(2), 385–390.

Foo, K. Y., & Hameed, B. H. (2011b). Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted $K_2CO_3$ activation. *Bioresource Technology*, *102*(20), 9794–9799.

Hameed, B. H., Ahmad, A. L., & Latiff, K. N. A. (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and Pigments*, *75*(1), 143–149.

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. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1597–1607.

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. *Applied Microbiology and Biotechnology*, *45*(6), 764–770.

Hu, Z., & Vansant, E. F. (1995). Carbon molecular sieves produced from walnut shell. *Carbon*, *33*(5), 561–567.

Kazemipour, M., Ansari, M., Tajrobehkar, S., Majdzadeh, M., & Kermani, H. R. (2008). Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. *Journal of Hazardous Materials*, *150*(2), 322–327.

Kazmierczak-Razna, J., Gralak-Podemska, B., Nowicki, P., & 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.

Kienow, K. K. (1989). Sulfide in Wastewater Collection and Treatment Systems. CONF, ASCE.

Lussier, M. G., Shull, J. C., & Miller, D. J. (1994). Activated carbon from cherry stones. *Carbon*, *32*(8), 1493–1498.

Martins, A. C., Pezoti, O., Cazetta, A. L., Bedin, K. C., Yamazaki, D. A. S., Bandoch, G. F. G., … Almeida, V. C. (2015). Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium studies. *Chemical Engineering Journal*, *260*, 291–299.

Montgomery, D. C. (2001). Design and analysis of experiments Fifth Edition. By John Wiley & Sons. *Inc. All Rights Reserved*.

Nowicki, P., Skibiszewska, P., & Pietrzak, R. (2013). $NO_2$ removal on adsorbents prepared from coffee industry waste materials. *Adsorption-Journal of the International Adsorption Society*, *19*(2–4), 521–528.

Ozekmekci, M., Salkic, G., & Fellah, M. F. (2015). Use of zeolites for the removal of $H_2S$: A mini-review. *Fuel Processing Technology*, *139*, 49–60.

Pietrzak, R., & Bandosz, T. J. (2007). Activated carbons modified with sewage sludge derived phase and their application in the process of $NO_2$ removal. *Carbon*, *45*(13), 2537–2546.

Purcell, J. M., Juyal, P., Kim, D.-G., Rodgers, R. P., Hendrickson, C. L., & Marshall, A. G. (2007). Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray ionization Fourier transform ion cyclotron

resonance mass spectrometry. *Energy & Fuels*, *21*(5), 2869–2874.

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. R., & Lehmann, J. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils*, *48*(3), 271–284.

Roy, P., Mondal, N. K., & Das, K. (2014). Modeling of the adsorptive removal of arsenic: a statistical approach. *Journal of Environmental Chemical Engineering*, *2*(1), 585–597.

Rufford, T. E., Hulicova-Jurcakova, D., Khosla, K., Zhu, Z., & Lu, G. Q. (2010). Microstructure and electrochemical double-layer capacitance of carbon electrodes prepared by zinc chloride activation of sugar cane bagasse. *Journal of Power Sources*, *195*(3), 912–918.

Santoro, D., de Jong, V., & Louw, R. (2003). Hydrodehalogenation of chlorobenzene on activated carbon and activated carbon supported catalysts. *Chemosphere*, *50*(9), 1255–1260.

Sekirifa, M. L., Hadj-Mahammed, M., Pallier, S., Baameur, L., Richard, D., & Al-Dujaili, A. H. (2013). Preparation and characterization of an activated carbon from a date stones variety by physical activation with carbon dioxide. *Journal of Analytical and Applied Pyrolysis*, *99*, 155–160.

Shaaban, A., Se, S. M., Ibrahim, I. M., & Ahsan, Q. (2015). Preparation of rubber wood sawdust-based activated carbon and its use as a filler of polyurethane matrix composites for microwave absorption. *Xinxing Tan Cailiao/New Carbon Materials*, *30*(2), 167–175.

Tan, I. A. W., Ahmad, A. L., & Hameed, B. H. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials*, *153*(1–2), 709–717.

Treviño-Cordero, H., Juárez-Aguilar, L. G., Mendoza-Castillo, D. I., Hernández-Montoya, V., Bonilla-Petriciolet, A., & Montes-Morán, M. A. (2013). Synthesis and adsorption properties of activated carbons from biomass of Prunus domestica and Jacaranda mimosifolia for the removal of heavy metals and dyes from water. *Industrial Crops and Products*, *42*, 315–323.

Tsai, W. T., Lee, M. K., & Chang, Y. M. (2007). Fast pyrolysis of rice husk: Product yields and compositions. *Bioresource Technology*, *98*(1), 22–28.

Vollertsen, J., Nielsen, A. H., Jensen, H. S., Wium-Andersen, T., & Hvitved-Jacobsen, T. (2008). Corrosion of concrete sewers-the kinetics of hydrogen sulfide oxidation. *The Science of the Total Environment*, *394*(1), 162–70.

Wang, X., Zhu, N., & Yin, B. (2008). Preparation of sludge-based activated carbon and its application in dye wastewater treatment. *Journal of Hazardous Materials*, *153*(1), 22–27.

Yang, K., Peng, J., Srinivasakannan, C., Zhang, L., Xia, H., & Duan, X. (2010). Preparation of high surface area activated carbon from coconut shells using microwave heating. *Bioresource Technology*, *101*(15), 6163–6169.

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. *Separation and Purification Technology*, *45*(1), 50–60.