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Original Article

Modeling and optimization of ammonia treatment by acidic biochar using response surface methodology

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Abstract

Emission of ammonia (NH_3) contaminated waste air to the atmosphere without treatment has affected humans and environment. Eliminating NH_3 in waste air emitted from industries is considered an environmental requisite. In this study, optimization of NH_3 adsorption time using *acidic rubber wood biochar* (RWBs) impregnated with sulfuric acid (H_2SO_4) was investigated. The central composite design (CCD) in response surface methodology (RSM) by the Design Expert software was used for designing the experiments as well as the full response surface estimation. The RSM was used to evaluate the effect of adsorption parameters in continuous mode of fixed bed column including waste air flow rate, inlet NH_3 concentration in waste air stream, and H_2SO_4 concentration for adsorbent surface modification. Based on statistical analysis, the NH_3 symmetric adsorption time (at 50% NH_3 removal efficiency) model proved to be very highly significant ($p<0.0001$). The optimum conditions obtained were 300 ppmv inlet NH_3 concentration, 72% H_2SO_4, and 2.1 l/min waste air flow rate. This resulted in 219 minutes of NH_3 adsorption time as obtained from the predicted model, which fitted well with the laboratory verification result. This was supported by the high value of coefficient of determination ($R^2=0.9137$). $(NH_4)_2SO_4$, a nitrogen fertilizer for planting, was the by-product from chemical adsorption between NH_3 and H_2SO_4.

Keywords: response surface methodology (RSM), ammonia, adsorption, rubber wood, biochar

1. Introduction

Ammonia (NH_3), a colorless, pungent, and corrosive gas, is one of the most abundant nitrogen-containing compounds in the atmosphere, after nitrogen (N_2) and nitrous oxide (N_2O). The global production of NH_3 by human activities (e.g., combustion of nitrogen-containing biomass, fossil fuels, and use of NH_3-based fertilizers) is estimated to be 45.0 million tons per year. Ammonia can be smelt at as low a level as 50 ppmv in the air. Breathing levels of 50-100 ppmv NH_3 can give rise to eye, throat, and nose irritation. The US Occupational Safety and Health Administration (OSHA) has set a limit of 50 ppmv over an 8-hrs work day or 40-hrs work week for ammonia vapor in ambient air (Guo *et al.*, 2005).

It is important to find suitable technologies for controlling the NH_3 gas emission. The removal of NH_3 from waste air can be performed by many technologies such as catalytic decomposition, reaction of NH_3 with another gas, absorption, and incineration have been used to eliminate NH_3 emissions before emission into atmosphere (Guo *et al.*, 2005). Among these techniques, the removal of NH_3 using dry adsorbents (Guo *et al.*, 2005; Ciahotný *et al.*, 2006; Rodrigues *et al.*, 2007) is a promising approach that has attracted much attention due to its simplicity and economical feasibility in configuration and operation.

According to Rodrigues *et al.* (2007), NH_3 adsorption by activated carbon was studied; they found that more amounts of adsorbent had to be used for higher efficiency. Alternately, adsorbents impregnating with H_2SO_4 has been employed for chemical adsorption of NH_3 from the gas stream

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(Ciahotný *et al.*, 2006; Liang-hsing *et al.*, 2006) for increased NH_3 removal efficiency. Chemical reaction between NH_3 and H_2SO_4 in adsorption column is shown in Equation 1 (Liang-hsing *et al.*, 2006). The mechanism by which the NH_3 was removed from the waste air and reacted with H_2SO_4 can be noticed to consist of four steps in series: (1) NH_3 permeates from the waste gas stream to the external surface of the adsorbent support; (2) the adsorbed NH_3 diffuses to the pore mouth of the adsorbent; (3) the NH_3 molecules diffuse through a gas-liquid interface and dissolve in the aqueous H_2SO_4 layer; and (4) the aqueous NH_3 reacts with H_2SO_4. The reaction forms $(NH_4)_2SO_4$ crystals as a by-product which remains on the adsorbent that can be used as nitrogen fertilizer.

$$2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow (NH_4)_2SO_{4(s)} \quad (1)$$

Biochar is produced by thermal decomposition of biomass under limited or absence of oxygen supply at relatively low temperatures (< 700°C) (Yu *et al.*, 2011). Biochar can be used for various purposes, e.g. making pyrolysis gas filters, as a base product for production of nitrogen fertilizers and activated carbon, and the char also improves forest productivity (Dumroese *et al.*, 2011). From the various types of biomass resources, wood waste was preferably selected to produce biochar for this work. Rubber wood (*Hevea brasiliensis*) is grown in tropical areas and the economic life of the trees is 25-30 years; about 3-4% of the rubber tree in a growing area is cut down for replanting annually. The rubber wood residues comprise small branches left in the cut down of the plantation (54% of total biomass) and saw mill wastes (32%). On an annual basis, rubber wood residues in the form of saw dusts and wood off-cut is estimated at 4125×10^3 tons (Krukanont and Prasertsan, 2004). Tanghizadeh-Toosi *et al.* (2012), in a study of NH_3 adsorption onto pine wood biochar for reducing NH_3 volatilization from soil, have found that biochar could capture NH_3 from soil at an efficiency rate of 45% after utilizing it at 15 or 30 t ha^{-1}. Since capturing of NH_3 from soil is practicable using biochar, removal of NH_3 from foul air using biochar might also be possible. As for a suitable material to be produced as biochar, rubber wood is indigenous and abundant in Thailand, especially in southern Thailand, and hence it could be appropriately considered to be utilized likewise to other type of wood as previously reported elsewhere. Thus, rubber wood off-cut has been selected to be the precursor for biochar production in the present waste air treatment study.

Conventional and classical methods of studying a process by maintaining other factors involved at specified constant levels do not depict the combined effect of all the factors involved. Conventional technique for optimization of a multivariable system usually defines one factor at a time. Such a technique needs to perform a number of experiments and could not reveal the alternative effects between the components. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable. Recently, many statistical experimental design methods have been employed in chemical process optimization. Experimental design techniques are a very useful tool for this purpose as they provide statistical models, which help in understanding the interactions among the parameters that have been optimized. These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one of the suitable methods utilized in many fields. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications (Mahalik *et al.*, 2010). This method could effectively be used to form a process model and to predict results to achieve the optimal NH_3 removal efficiency of the adsorption column.

In the present study, rubber wood biochar has been used for the removal of NH_3 from waste air through an adsorption column. The efficiency of biochar can be increased by impregnation with H_2SO_4 in order to form acidic biochar. The central composite design (CCD), a design of experimental techniques, has been chosen to carry out the experiments at five levels in respect of an optimal criterion. Three operating factors were chosen as independent variables, namely, the effects of H_2SO_4 concentration for impregnation on biochar, NH_3 inlet concentration in waste air, and waste air flow rate. With response surface methodology, the interaction of possible influencing parameters on NH_3 removal efficiency can be evaluated. Graphical response surface and contour plots were used to localize the region of the optimum condition (Grutuito *et al.*, 2008; Kayet *et al.*, 2011).

2. Materials and Methods

2.1 Materials

Rubber wood biochar (RWB) was carbonized in a stainless steel tube reactor (length 50 cm and diameter 4 cm) under 4 l/min nitrogen at 500°C for 2 hrs. The carbon products was crushed and sieved to particle sizes of 2.36-3.36 mm. 95-97% H_2SO_4 and 25% NH_3 solution analytical grade were obtained from Merck. The H_2SO_4 acid was used as an impregnating reagent for acidic rubber wood biochar preparation. NH_3 solution was applied for generating NH_3 vapor to produce simulated waste air by mixing it with the air stream from an air compressor.

2.2 Acidic adsorbent preparation and characterization

The acidic rubber wood biochar was prepared by contacting 2 g of dried RWB into 10 ml of known H_2SO_4 concentration. Upon soaking time of 1 h at room temperature (28-29°C), the samples were filtrated by a vacuum filter then

dried in hot air oven at 110°C for 1 h and cooled down in glass desiccators. Microscopic images of RWBs were obtained by scanning electron microscope (JSM-5200). The SEM enables direct observation of the changes in the surface microstructures of the adsorbent due to the adsorption NH_3. BET surface area of the sample were determined by nitrogen adsorption at -196°C with sorptiometer (Surface Area and Pore Size Analyzers, COULTER™ SA3100™).

2.3 Adsorption experiments

The adsorption capacities of RWBs were tested in laboratory scale of continuous down-flow fixed-bed column. The schematic diagram of NH_3 contaminated waste air generation and adsorption unit are depicted in Figure 1. The adsorption column was a glass with an inside diameter of 2 cm and a column height of 15 cm. Fiber glass was installed in the bottom part of the column to support RWBs.

Waste air stream with NH_3 contamination was prepared for the adsorption test by passing air flow from an air compressor through a NH_3 reservoir. NH_3 solution of 25% was filled in the reservoir to pick up the vaporized NH_3 gas and mix with the air stream at room temperature (28-29°C). The mixing stream was forced to flow through the mixing tank under continuous and steady flow to the adsorption column.

2.4 Air samples analysis

In the experiment, air samples were taken by a sampling pump (224- PCXR8 Air Sampling Pump, SKC Inc.). The air/ammonia gaseous mixture was bubbled through a 50 ml cold boric acid solution in an impinger (a glass gas wash bottle) at 2 l/min for 1 min. NH_3 absorbed was measured by titration method using 0.2% mixed indicators (methyl red and methylene blue) (American Public Health Association, 1995) and calculated for NH_3 concentration in simulated waste air

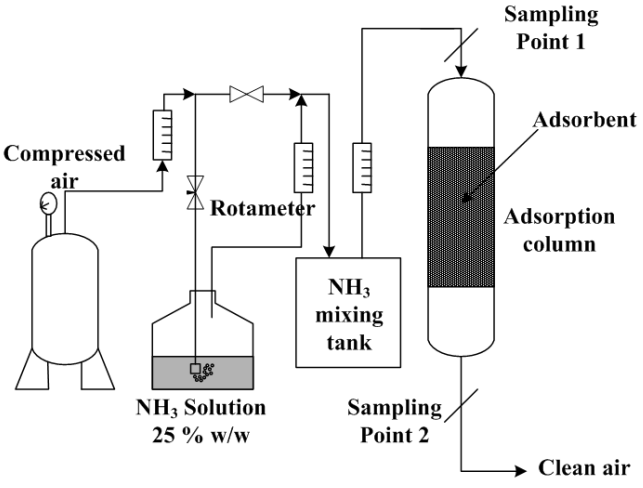


Figure 1. Schematic diagram of NH_3 contaminated waste air generation and treatment system.

(Rodrigues *et al.*, 2007). The percentage of NH_3 removal efficiency was calculated by Equation 2 through NH_3 concentration of inlet and outlet stream.

$$\text{Eff.}(\%) = \frac{C_i - C_o}{C_i} \times 100 \quad (2)$$

where C_i and C_o are NH_3 concentration (ppmv) in the inlet and outlet air streams of adsorption column. Eff. (%) is the percentage of NH_3 removal efficiency.

NH_3 concentrations of the inlet and outlet waste air stream were measured every 10 min until the concentrations of both streams were equal, thus demonstrating the saturation of the adsorbent bed. When saturation was achieved, the experiment was stopped and the adsorbent bed was disassembled.

2.5 Experimental design and analysis

Basically, an optimization process involves three major steps, which are (1) performing the statistically designed experiments, (2) estimating the coefficients in a mathematical model, and (3) predicting the response and checking the adequacy of the model (Mahalik *et al.*, 2010), as with the set up in this experiment. Central composite design has been applied in this work to study the design of the NH_3 adsorption experiments. CCD has been widely used for fitting a second-order model from experimental runs. The design consists of a 2^n factorial or fraction (coded to the usual ±1 notation) augmented by 2n axial points ($\pm\alpha$, 0, 0,..., 0), (0, $\pm\alpha$, 0,..., 0),..., (0, 0,..., $\pm\alpha$), and n_c center points (0, 0, 0,..., 0). In this case, the main effects and interactions may be estimated by fractional factorial designs running only a minimum number of experiments. The responses and the corresponding parameters were modeled and optimized using analysis of variance (ANOVA) to estimate the statistical parameters by means of RSM. If all variables are assumed to be measurable, the response surface can be expressed, in Equation 3, as follows.

$$Y = f(X_1, X_2, X_3, X_4....., X_n) \quad (3)$$

where Y is the response of the system and X_i is the variables of action called factors. The goal of the RSM is to optimize the response variable (Y) and search for a suitable approximation of the functional relationship between the independent variables and the response surface. It is assumed that the independent variables are continuous and controllable by experiments with negligible errors.

The symmetric adsorption time ($t_{1/2}$) of biochar adsorbent is defined as the ideal time at a proportion of 50% NH_3 adsorption efficiency for an operating curve or breakthrough curve at $C_i/C_o = 0.5$ (McCabe *et al.*, 2005). The operating curves can be plotted between NH_3 adsorption efficiency versus operating time of waste air flowed through the bed. The $t_{1/2}$ can represent the adsorption capacity of the adsorbent and can be used for design of the adsorption column.

Then the $t_{1/2}$ was applied for the response of adsorption data in the RSM solution to develop an empirical model that is correlated to the three-process variables. NH_3 inlet concentration in waste air feeding, H_2SO_4 concentration for adsorbent preparation, and waste air flow rate were chosen as designed variables. Second degree quadratic equation as given by Equation 4 (Rajasimman and Murugaiyan, 2010) was used for model formation. Applying the relationships in Table 1, the values of the codes were calculated and shown in Table 2.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \left(\sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j\right)_{i<j} \quad (4)$$

where Y is the predicted response evaluated, x_i and x_j are the variables, β_0 is the constant coefficient, β_i, β_{ii} and β_{ij} are the inter-action coefficients of linear, quadratic, and the second-order terms, respectively, and *k* is the number of studied factors.

For statistical analysis, the experimental variables X_i have been coded as x_i according to the following Equation 5.

$$x_i = \frac{(X_i - X_n)}{\Delta X_i} \quad (5)$$

where x_i is the coded value (dimensionless) of the i^{th} independent variable, X_i is the uncoded value of the i^{th} independent variable, is the X_i at the center point, and ΔX_i is the step change value of the real variable i.

From Equation 5, the coded unit can be converted to the uncoded unit.

The total number of tests (N_t) required for the three independent variables are shown in Equation 6.

$$N_t = 2^n + 2n + n_c = 2^3 + (2 \times 3) + 3 = 17 \quad (6)$$

The number of tests require for the CCD includes the standard 2^n factorial with its origin at the center, 2n points fixed axially at a distance, say a, from the center to generate the quadratic terms, and replicate tests at the center (n_c=3), where n is the number of dependent variables. The axial points are chosen in such a manner that they allow rotatability, which ensures that the variance of the model prediction is constant at all points equidistant from the design center. Replicates of the test at the center are very important as they provide an independent estimate of the experimental error.

The quality of the fit of the polynomial model was expressed by the value of correlation coefficient (R^2) (Jain *et al.*, 2011). The experimental plan was generated using the Design-Expert program 8.0.6 trial version (Stat-Ease Inc., Minneapolis, USA). Finally, the optimum values for maximizing the amount of the studied responses were determined using the same Design-Expert software (Bashir *et al.*, 2011; Montgomery *et al.*, 2005).

3. Results and Discussions

3.1 Adsorption studies

NH_3 adsorption efficiency from waste air by acidic rubber wood biochar adsorbent in our work is at 90% (from 300 ppmv down to 30 ppmv). Since OSHA has set a permissible exposure limit concentration of 50 ppmv over an 8-hrs work day or a 40-hrs work week period for ammonia vapor in

Table 1. Relation between coded value and level of the variable (Mahalik *et al.*, 2010).

Coded value	Level of variable
$-\alpha$	X_{min}
-1	$[(X_{max}+X_{min})/2]-[(X_{max}-X_{min})/2\beta]$
0	$(X_{max}+X_{min})/2$
+1	$[(X_{max}+X_{min})/2]+[(X_{max}-X_{min})/2\beta]$
$+\alpha$	X_{max}

Where X_{max} and X_{min} are maximum and minimum values of X, respectively; β is $2^{n/4}$
n = number of variables (in this study; $\beta = 2^{3/4} = 1.682$).

Table 2. Independent variables and their levels for CCD experimental design.

Independent Variables	Symbol	Coded variable levels				
		$-\alpha$	-1	0	+1	$+\alpha$
NH_3 inlet concentration (ppmv)	X_1	300	645	1150	1655	2000
H_2SO_4 concentration (%)	X_2	40	48	60	72	80
Waste air flow rate (l/min)	X_3	2	2.6	3.5	4.4	5

ambient air (Guo *et al.*, 2005), our NH_3 outlet concentration resulted from a treatment of a quite high inlet waste air concentration is appreciably within OSHA standards.

From the experimental design table, we could present the adsorption capacity and determine the symmetric adsorption time of each run by plotting the operating line and breakthrough curve. The intersection between the operating line and the breakthrough curve generated the coordinate (50% Eff., $t_{1/2}$), which was a relatively straightforward approach to determine $t_{1/2}$. Figure 2 shows the operating line and the breakthrough curve at experimental conditions of 1,150 ppmv inlet NH_3 concentration, 80% H_2SO_4 concentration, and 3.5 l/min waste air flow rate.

Figure 3 presents the SEM surface images of RWBs at, before, and after NH_3 adsorption performed in the continuous waste air flow adsorption system. The initial RWBs, seen in Figure 3a, shows a perfect honeycombed structure with clear opening of pores and thick walls, with a BET surface area of 2.22 m^2/g. After NH_3 adsorption, shown in Figure 3b, the honeycombed structure was covered by crystals of $(NH_4)_2SO_4$ and the BET surface area decreased to 0.22 m^2/g.

3.2 ANOVA analysis and fitting of quadratic model

The statistical software package 'Design Expert' has been used for regression analysis of the experimental data and to draw the response surface plot. ANOVA was used to estimate the statistical characteristics of the model fitting. The complete experimental design and results consisting of coded levels, actual variables, and responses are given in Table 3. In order to ensure a good model, a test for significance of the regression model and individual model coefficients was needed to be performed accompanying with the lack-of-fit test. Normally, the significant factors can be ranked based on the F-value or p-value (also named 'Prob. > F' value). The larger the magnitude of the F-value and correspondingly the smaller the 'Prob. > F' value, the more significant is the corresponding coefficient (Yi *et al.*, 2010).

As there are many insignificant model terms from the full second quadratic model, they can be sorted out and then an improved model could be obtained. Thus, with the Design Expert program, the stepwise elimination procedure was selected to automatically eliminate the insignificant terms. The resulting ANOVA data for the reduced quadratic model of total flux are given in Table 4. By applying multiple regression analysis on the experimental data, the reduced quadratic equation in terms of code factors was obtained, as shown in Equation 7.

$$t_{1/2} = 44.90 - 26.42\,X_1 + 11.98\,X_2 - 19.64\,X_3 + 15.63\,X_1X_3 + 15.28\,X_1^2 \quad (7)$$

where $t_{1/2}$ is the symmetric adsorption time. X_1, X_2, and X_3 are the NH_3 inlet concentration, H_2SO_4 concentration, and waste air flow rate, respectively, detailed in Table 2.

From Table 4 and Equation 7, significant terms for the response surface model can be determined. Firstly, the linear terms of the NH_3 inlet concentration (X_1), and the waste air flow rate (X_3) have the largest negative effects on $t_{1/2}$, followed by H_2SO_4 concentration (X_2), which has a positive effect. The second order term of NH_3 inlet concentration (X_1^2) and the interaction of X_1 and X_3 are also significant terms in the model. Ranking of these significant terms is as follows, with $X_1 > X_3 > X_1^2 > X_2 > X_1X_3$. The predicted R^2 of

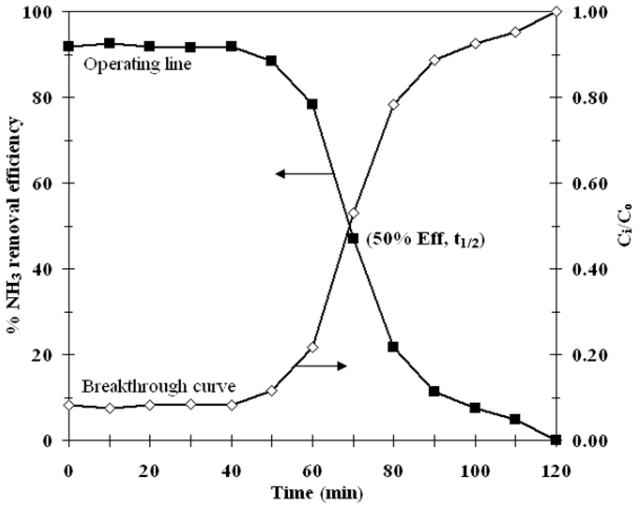
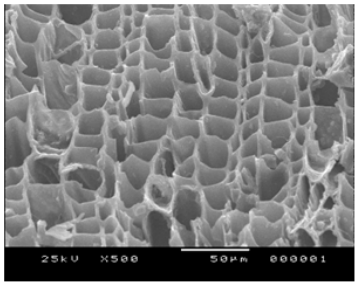
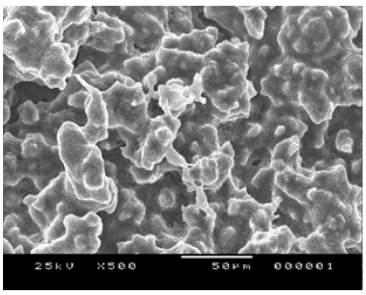


Figure 2. Correlation between operating line and breakthrough curve for symmetric adsorption time ($t_{1/2}$) determination in NH_3 adsorption system by biochar adsorbent.



(a)



(b)

Figure 3. SEM photographs (500x) of RWBs before (a) and after (b) NH_3 adsorption in a continuous waste air flow adsorption system.

Table 3. Central composite design consisting of experiments for the study of experimental factors in coded and actual values with responses from experimental results.

Standardrun no.	Run	Coded values			Actual values			Response values
		X_1	X_2	X_3	X_1 (ppmv)	X_2 (%)	X_3 (l/min)	$t_{1/2}$ (min)
1	15	-1	-1	-1	645	48	2.6	125
2	4	+1	-1	-1	1655	48	2.6	38
3	14	-1	+1	-1	645	72	2.6	148
4	11	+1	+1	-1	1655	72	2.6	56
5	2	-1	-1	+1	645	48	4.4	35
6	17	1	-1	+1	1655	48	4.4	22
7	16	-1	+1	+1	645	72	4.4	75
8	1	+1	+1	+1	1655	72	4.4	34
9	3	-α	0	0	300	60	3.5	117
10	13	+α	0	0	2000	60	3.5	41
11	12	0	-α	0	1150	40	3.5	28
12	10	0	+α	0	1150	80	3.5	70
13	7	0	0	-α	1150	60	2.0	65
14	6	0	0	+α	1150	60	5.0	25
15	5	0	0	0	1150	60	3.5	30
16	9	0	0	0	1150	60	3.5	32
17	8	0	0	0	1150	60	3.5	31

Table 4. ANOVA table (partial sum of squares) for reduce quadratic model.

Source	Sum of squares	DF	Mean Square	F-value	Prob > F	Remarks
Model	21757.20	5	4351.44	23.29	<0.0001	significant
X_1	9532.82	1	9532.82	51.02	<0.0001	significant
X_2	1960.66	1	1960.66	10.49	0.0079	significant
X_3	5269.86	1	5269.86	28.20	0.0002	significant
X_1X_3	1953.13	1	1953.13	10.45	0.0080	significant
X_i^2	3040.73	1	3040.73	16.27	0.0020	significant
Residual	2055.27	11	186.84			
Lack of Fit	2053.27	9	228.14	228.14	0.0044	significant
Pure Error	2.00	2	1.00			
Correlation Total	23812.47	16				
Standard deviation	13.67		R^2	0.9137		
Mean	57.18		Adjusted R^2	0.8745		
C.V.(%)	23.91		Predicted R^2	0.7749		
PRESS	5359.06		Adequate Precision	15.0216		

[a] DF = Degree of freedom
[b] C.V. = Coefficient of variation
[c] PRESS = Predicted residual sum of squares

0.7749 is in reasonable agreement with the adjusted R^2 of 0.8745. The value of adequate precision is 15.0216, which is well above 4.

The application of the response surface methodology yields, on the basis of parameter estimates, an empirical relationship between the response variables (the symmetric adsorption time, $t_{1/2}$) and the test variables. These are related to the following quadratic expression in code unit, and after substituting Equation 7 to the refined model, the final model in terms of natural variables are obtained, as represented below:

$$t_{1/2} = 340.2598 - (0.3111 \times \text{initial } NH_3 \text{ concentration}) + (1.0076 \times H_2SO_4 \text{ concentration}) - (61.8859 \times \text{waste air flow rate}) + (0.0347 \times \text{initial } NH_3 \text{ concentration} \times \text{waste air flow rate}) + (0.0001 \times \text{initial } NH_3 \text{ concentration}^2) \quad (8)$$

The quadratic equation obtained with multiple variables can be used to predict the $t_{1/2}$ within the limits of the experimental factors. Figure 4 reveals that the predicted response values of the reduced quadratic model are well in agreement with the actual ones in the range of the operating variables.

3.3 Combined effect of operating parameters on the response

In order to visualize the relationship between the experimental variables and the response, and to study individual and interaction effects of the three factors consisting of the inlet NH_3 concentration, the H_2SO_4 concentration, and the waste air flow rate on the symmetric adsorption time ($t_{1/2}$) of NH_3 adsorption, response surfaces and contour plots were generated from the final model, as shown in Figure 5, and the contours were plotted in the x-y plane by a projection of the response surface (Amari *et al.*, 2008). These figures illustrate the response of different experimental variables and can be used to identify the major interactions between the variables. Each contour curve represents an infinite number of combinations of two test variables. Other factors are kept each time at their respective zero levels (Amari *et al.*, 2008). A careful observation of the ANOVA results reveals that the inlet NH_3 concentration, the H_2SO_4 concentration, and the waste air flow rate have affected the response of the symmetric adsorption time for NH_3 treatment. However, the inlet NH_3 concentration imposes the greatest effect while the H_2SO_4 concentration imposes the least. On the other hand, the quadratic effect of inlet NH_3 concentration and the interaction effect of inlet NH_3 concentration and waste air flow rate impose also significant effects to the symmetric adsorption time of NH_3 treatment.

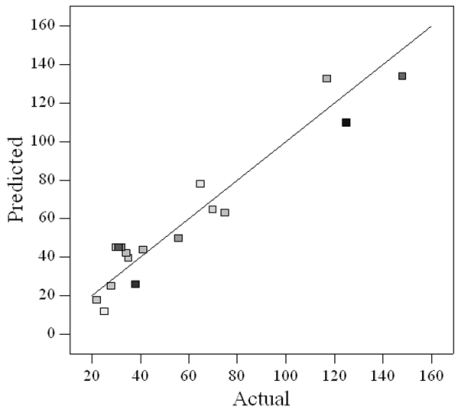


Figure 4. Plot of predicted response vs. actual value for $t_{1/2}$ response from reduced surface quadratic model.

By keeping the waste air flow rate at 3.5 l/min, the combined effect of the inlet NH_3 concentration (X_1) and the H_2SO_4 concentration (X_2) was investigated as shown in a 3D surface and its corresponding contour plotted in Figure 5a-b. As it can be seen, the $t_{1/2}$ response decreases when the inlet NH_3 concentration changes from 300 ppmv to 2,000 ppmv. The slope of the response surface is more negatively inclined with increasing inlet NH_3 concentration according to the additional term of x_i^2 in the quadratic model. The high NH_3 concentration generated more $(NH_4)_2SO_4$ crystals at the pore mouth which then reduced the adsorption area with an effect on the decrease in $t_{1/2}$. With the increase of H_2SO_4 concentration on the rubber wood biochar surface, $t_{1/2}$ also increased because the higher H_2SO_4 concentration on RWB surface increased the amount of H_2SO_4 reactant to react with NH_3 in the gas phase (Liang-hsing *et al.*, 2006). Thus NH_3 gas could be more removed from the waste air with more generation of $(NH_4)_2SO_4$. The elliptical contour plot shows that the interaction term of X_1X_2, which indicates the higher H_2SO_4 concentration and lower inlet NH_3 concentration, has affected higher adsorption. The maximal $t_{1/2}$ of 182 min was obtained at 300 ppmv inlet NH_3 concentration and 80% H_2SO_4 concentration.

Figure 5c-d depicts the 3D plot and its corresponding contour plot to show the effects of H_2SO_4 concentration (X_2) and waste air flow rate (X_3) on $t_{1/2}$ response while keeping inlet NH_3 concentration (X_1) at 1150 ppmv. The graph shows that the maximum $t_{1/2}$ at 121 min occurs at 80% H_2SO_4 concentration and 2 l/min waste air flow rate, which is in accordance with the model. Increasing the H_2SO_4 concentration, from 40% to 80%, increased the $t_{1/2}$. It is very clear that H_2SO_4 concentration on the biochar surface has affected the NH_3 adsorption time. Increasing the waste air flow rate from 2 to 5 l/min, the $t_{1/2}$ was reduced. In consequence of higher waste air flow rate, the contact time between NH_3 in waste air and H_2SO_4 on the RWB surface was shortened, thus crystals from the reaction between NH_3 in the waste air and H_2SO_4 generated rapidly and covered the surface and the pore mouths of the RWB and hence the active sites on the surface were lessened, resulting in lower adsorption efficiency.

The combined effect of inlet NH_3 concentration (X_1) and waste air flow rate (X_3) has been analyzed. The $t_{1/2}$ from the response surface quadratic model, keeping H_2SO_4 concentration at 60%, is shown in the 3D surface plot and its corresponding contour plot in Figure 5e and 5f, respectively. It can be observed that the slope of each contour curve of the waste air flow rate entirely depends on the inlet NH_3 concentration. The higher the waste air flow rate and the inlet NH_3 concentration, the lower the adsorption that could be obtained. This indicates that the interaction effect between the waste air flow rate and the inlet NH_3 concentration is greatly pronounced, as confirmed by the significant test of the interaction term (X_1X_3) in the adsorption model. Because at higher waste air flow rate the retention time on the rubber wood biochar was short and higher NH_3 loading produced higher amounts of NH_3 to react with H_2SO_4 on the surface;

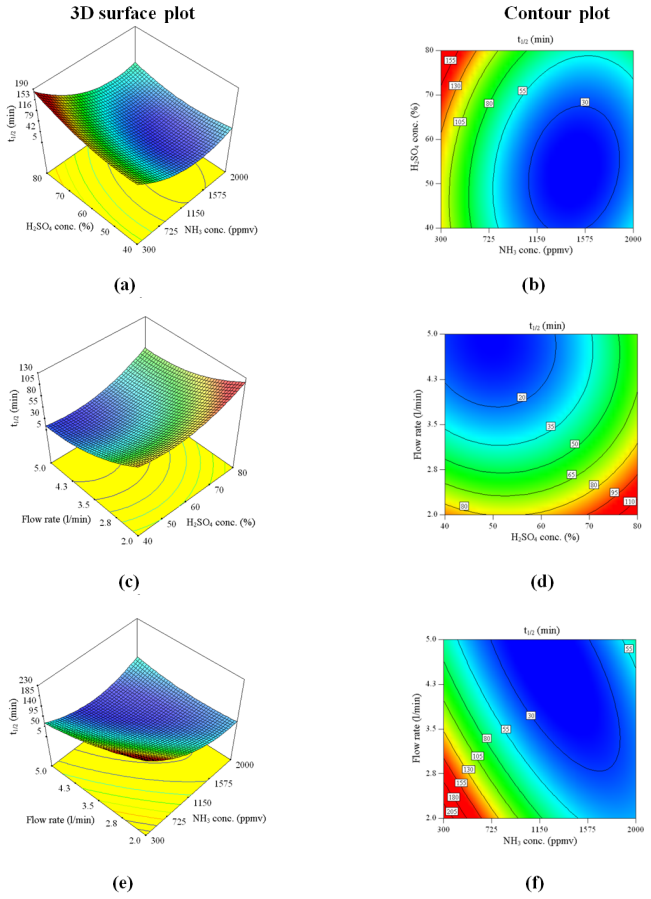


Figure 5. 3D surface and contour plotted for a combined effect of a,b) inlet NH_3 concentration and H_2SO_4 concentration of 3.5 l/min, c,d) H_2SO_4 concentration and waste air flow rate for 1,150 ppmv NH_3, e,f) NH_3 concentration and waste air flow rate under 60% H_2SO_4, on $t_{1/2}$ in the NH_3 adsorption system.

$(NH_4)_2SO_4$ crystals were immediately generated to cover the reactive surface and hence the adsorption areas were reduced with an effect in the drop of $t_{1/2}$. The maximum $t_{1/2}$ observed was 223 min when the inlet NH_3 concentration was 300 ppmv and the waste air flow rate was 2 l/min.

3.4 Process optimization using response surface methodology

The optimum condition of NH_3 adsorption system was obtained using numerical optimization feature of the Design Expert software (Bhatia *et al.*, 2009). The program searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The reduced quadratic model was applied to determine the optimum condition for the response of $t_{1/2}$. The inlet NH_3 concentration of 300 ppmv was chosen and fixed for the NH_3 adsorption system because it is the level of NH_3 (200-300 ppmv) emitting in many industrial work places (Pollution Control Department, 2005).

The most desirable experimental condition suggested by the software was selected for optimum condition to maximize the symmetric adsorption time ($t_{1/2}$). The predicted symmetric adsorption time for NH_3 adsorption from the waste air was at 219 min. The optimum result was verified by using 2 g of acidic biochar for adsorbing NH_3 from the waste air in a continuous adsorption unit according to experimental conditions given in Table 5. The verified experimental result of the symmetric adsorption time was at 220 min. It could be observed that the experimental value obtained from the adsorption system using biochar was in very good agreement with the value calculated from the model (Table 5).

For direct comparison, a similar testing procedure was also applied on activated carbon commercial grade (AC; CGC–11A in granular form with surface area of 1,000-1,100 m^2/g, purchased from Qualitech Supply Ltd., Part., Songkhla, Thailand) Moreover, AC had been impregnated with H_2SO_4 to be acidic activated carbon (ACs). The result of breakthrough curve of NH_3 adsorption of 300 ppmv from waste air flow rate 2.1 l/min by AC and RWB, the data can be plotted as shown in Figure 6.

From Figure 6, by comparing the NH_3 breakthrough curves of no-impregnation adsorbents (AC and RWB) with the sulphuric acidic adsorbents (ACs and RWBs), it is obvious that NH_3 adsorption time of acidic adsorbents were much greater, and hence H_2SO_4 impregnation is a must. For either no-impregnated or impregnated adsorbent, the adsorption time of AC was slightly greater than RWB for the former, and the adsorption time of ACs was slightly greater than RWBs for the latter, meaning the use of AC is slightly better than the use of RWB. However, RWB is three times cheaper than AC and the use of indigenous rubber wood biomass at an expense of slightly inferior adsorption property, instead of commercially available AC, can also render value-added aspect to the local product.

NH_3 adsorption capacity was calculated by the integration of the breakthrough curves (Rodrigues *et al.*, 2007). Comparison with those of some other adsorbents reported in

Table 5. Optimum condition and model validation of NH_3 adsorption system using acidic rubber wood biochar adsorbent.

NH_3 conc. (ppmv)	H_2SO_4 conc. (%)	Flow rate (l/min)	Symmetric adsorption time, $t_{1/2}$ (min)	
(X_1)	(X_2)	(X_3)	Predicted	Experimental
300	72	2.1	219	220

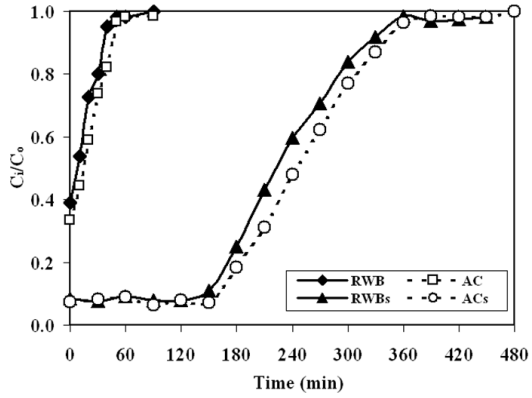


Figure 6. Breakthrough curve of NH_3 adsorption from waste air for comparison study between AC and RWB (without acid impregnation) and ACs and RWBs (with sulfuric acid impregnation).

the literature is given in Table 6. The value for NH_3 adsorption observed in this work is in good agreement with values found by other researches. Differences of NH_3 uptake are due to the properties of each adsorbent and experimental conditions.

Table 6 details a literature review comparing some selective adsorbents that have been studied and reported. In general, adsorbents without acid impregnation yield markedly lower efficiency than those with acid impregnation. Activated carbon with nitric acid impregnation exhibited a slightly lower adsorption capacity than that impregnated with sulfuric acid. RWB impregnated with sulfuric acid showed a capacity value in between, with a tendency towards the higher end, and thus can be considered one of the top choices for adsorbents.

4. Conclusion

In the present study, optimization of NH_3 removal from waste air with acidic rubber wood biochar was investigated to maximize the symmetric adsorption time in a continuous NH_3 adsorption system. The NH_3 treatment process optimization focused on the influence of individual, as well as the interaction effect variables, such as inlet NH_3 concentration, H_2SO_4 concentration, and waste air flow rate, employing response surface methodology with central composite design. The multiple correlation coefficient of determination R^2 obtained was 0.9137, inferring that the actual data fit quite well with the predicted data applying the quadratic model. Regression analysis, ANOVA, and response surface plots were conducted using the Design Expert Software for predicting the responses in the experiment. The derived optimum condition for NH_3 adsorption by RWBs to yield the symmetric adsorption time at 219 min was an impregnation with 72% H_2SO_4 for removing NH_3 at 300 ppmv inlet concentration and 2.1 l/min waste air flow rate. By applying these parameter values, the maximal symmetric adsorption time has been predicted and confirmed experimentally. The by-product from the reaction between NH_3 and H_2SO_4 is $(NH_4)_2SO_4$ crystals, which can be used as nitrogen fertilizer for plantation.

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Table 6. Comparison of NH_3 adsorption capacity of various adsorbents reported in literatures.

Adsorbent	Adsorption capacity (mg g^{-1})	Reference
Natural clinoptilolite	12.70	Ciahotný *et al.* (2006)
Modified clinoptilolite impregnated with acid	27.60-31.50	Ciahotný *et al.* (2006)
Activated carbon	0.60-1.80	Rodrigues *et al.* (2007)
Activated carbon impregnated with nitric acid	41.65	Huang *et al.* (2008)
Activated carbon impregnated with sulfuric acid	18.7-20.6	Canals-Batlle *et al.* (2008)
Rubber wood biochar impregnated with sulfuric acid	46.35	This work

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