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

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Abstract

Emission of ammonia (NH₃) contaminated waste air to the atmosphere without treatment has affected human and environment. Eliminating NH₃ in waste air emitted from industries is considered an environmental requisite. In this study, optimization of NH₃ adsorption time using acidic rubber wood biochar (RWBs) impregnated with sulfuric acid (H₂SO₄) 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 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 NH₃ concentration in waste air stream, and H₂SO₄ concentration for adsorbent surface modification. Based on statistical analysis, the NH₃ symmetric adsorption time (at 50% NH₃ removal efficiency) model proved to be very highly significant (p<0.0001). The optimum conditions obtained were 300 ppmv inlet NH₃ concentration, 72% H₂SO₄, and 2.1 l/min waste air flow rate. This resulted in 219 minutes of NH₃ adsorption time as obtained from the predicted model, which fitted well with the laboratory verification result. This was evidenced by the high value of coefficient of determination (R² = 0.9137). (NH₄)₂SO₄, a nitrogen fertilizer for planting, was the by-product from chemical adsorption between NH₃ and H₂SO₄.
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$_2$O). 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-h work day or 40-h work week for ammonia vapor in ambient air (Guo et al., 2005).

It is important to find the 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 (Rodrigues et al., 2007; Guo et al., 2005; Ciahotný et al., 2006) is a promising approach that has attracted much attention due to its simplicity and economy 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$_2$SO$_4$ has been employed for chemical adsorption of NH$_3$ from the gas stream (Liang-hsing et al., 2006; Ciahotný et al., 2006) for increased NH$_3$ removal efficiency. Chemical reaction between NH$_3$ and H$_2$SO$_4$ 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$_2$SO$_4$ 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$_2$SO$_4$ layer; (4) the aqueous NH$_3$ reacts with H$_2$SO$_4$. The reaction forms (NH$_4$)$_2$SO$_4$ crystal as by-product which remains on the adsorbent that can be used as nitrogen fertilizer.

\[
2\text{NH}_3(g) + \text{H}_2\text{SO}_4(aq) \rightarrow (\text{NH}_4)_2\text{SO}_4(s)
\]  

(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 in various activities such as the making of 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 forms of saw dusts and wood off-cut is estimated at $4125 \times 10^3$ tons (Krukanont and Prasertsan, 2004). Tanghizadeh-Toosi et al. (2012), in the 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 should also be possible. As for 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 lot 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 technique is a very useful tool for this purpose as it provides 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$_2$SO$_4$ to form acidic biochar. The central composite design (CCD), a design of experiment technique, had 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$_2$SO$_4$ concentration for impregnation on biochar, NH$_3$ inlet concentration in waste air, and waste air flow rate.

With response surface methodology (RSM), 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 i.d. 4 cm) under 4 l/min nitrogen at 500°C for 2 h. The carbon products was crushed and sieved to particle size of 2.36-3.36 mm. 95-97% H$_2$SO$_4$ and 25% NH$_3$ solution analytical grade were obtained from Merck. The H$_2$SO$_4$ acid was
used as an impregnating reagent for acidic rubber wood biochar (RWBs) preparation. 
NH$_3$ solution was applied for generating NH$_3$ vapor to produce simulated waste air by mixing with air stream from an air compressor.

2.2 Acidic adsorbent preparation and characterization

The acidic rubber wood biochar (RWBs) was prepared by contacting 2 g of dried RWB into 10 ml of known H$_2$SO$_4$ concentration. Upon soaking time of 1 h at room temperature (28-29°C), the samples was 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.

Figure 1.

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. NH₃ absorbed was measured by titration method using 0.2% mixed indicators
(methyl red and methylene blue) (American Public Health Association, 1995) and
calculated for NH₃ concentration in simulated waste air (Rodrigues et al., 2007). The
percentage of NH₃ removal efficiency was calculated by Equation 2 through NH₃
concentration of inlet and outlet stream.

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

where Cᵢ and Cₒ are NH₃ concentration (ppmv) in the inlet and outlet air streams of
adsorption column. Eff. (%) is the percentage of NH₃ removal efficiency.

NH₃ concentrations of the inlet and outlet waste air stream were measured every
10 min until concentrations of both streams were the same, 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;
performing the statistically designed experiments, estimating the coefficients in a
mathematical model, and 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 (CCD) has been applied in this work to study for the design of 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 $\pm 1$ 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.

$$Y = f (X_1, X_2, X_3, X_4, ..., X_n)$$ (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$_2$SO$_4$ 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.

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

where $Y$ is the predicted response evaluated; $x_i$ and $x_j$ are the variables; $\beta_0$ is the constant coefficient; $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are the interaction coefficients of linear, quadratic, and the second-order terms, respectively; and $k$ is the number of studied factors.

Table 1.

Table 2.

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

$$x_i = \frac{(X_i - X_0)}{\Delta X_i}$$  \hspace{1cm} (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, $X_0$ is the $X_i$ at the center point, and $\Delta X_i$ is the step change value of the real variable $i$.

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

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

$$N_t = 2^n + 2n + n_c = 2^3 + (2 \times 3) + 3 = 17$$  \hspace{1cm} (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 $\alpha$, 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 (Montgomery et al., 2005 and Bashir et al., 2011).
3. Results and Discussions

3.1 Adsorption studies

NH₃ adsorption efficiency from waste air by acidic rubber wood biochar adsorbent in our work is at 90% (from 300 ppmv down to 30 ppmv). And since OSHA has set a permissible exposure limit concentration of 50 ppmv over an 8-h work day or a 40-h work week period for ammonia vapor in ambient air (Guo et al., 2005), our NH₃ outlet concentration resulted from a treatment of a quite high inlet waste air concentration is appreciably within OSHA standard.

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., t₁/₂) and was a relatively straightforward approach to determine t₁/₂. Figure 2 shows the operating line and the breakthrough curve at experimental conditions of 1150 ppmv inlet NH₃ concentration, 80% H₂SO₄ concentration, and 3.5 l/min waste air flow rate.

Figure 2.

Figure 3 presents the SEM surface images of RWBs at, before, and after NH₃ 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 m²/g. After NH₃ adsorption, shown in Figure 3b, the honeycombed structure was covered by crystals of (NH₄)₂SO₄ and the BET surface area decreased to 0.22 m²/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 F-value and correspondingly the smaller the “Prob. > F” value, the more significant is the corresponding coefficient (Yi et al., 2010).

Table 3.

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 8.0.6 trial version, 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.

\[
t_{1/2}=44.90-26.42 X_1+11.98 X_2-19.64 X_3+15.63 X_1 X_3+15.28 X_1^2
\]  (7)
where $t_{1/2}$ is the symmetric adsorption time. $X_1$, $X_2$, and $X_3$ are, respectively, the NH$_3$ inlet concentration, H$_2$SO$_4$ concentration, and waste air flow rate 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 largest negative effects on $t_{1/2}$, followed by H$_2$SO$_4$ 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: $X_1 > X_3 > X_1^2 > X_2 > X_1X_3$. The predicted $R^2$ of 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:

$$t_{1/2} = 340.2598 - (0.3111 \times \text{initial NH}_3 \text{ concentration}) + (1.0076 \times \text{H}_2\text{SO}_4 \text{ concentration}) - (61.8859 \times \text{waste air flow rate}) + (0.0347 \times \text{initial NH}_3 \text{ concentration} \times \text{waste air flow rate}) + (0.0001 \times \text{waste air flow rate}^2) \hspace{1cm} (8)$$

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$_2$SO$_4$ 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 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 ANOVA results reveals that the inlet NH$_3$ concentration, the H$_2$SO$_4$ concentration, and the waste air flow rate have affected the response of symmetric adsorption time for NH$_3$ treatment. However, the inlet NH$_3$ concentration imposes the greatest effect while the H$_2$SO$_4$ 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.

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$_2$SO$_4$ concentration ($X_2$) was investigated as shown in
3D surface and its corresponding contour plotted in Figure 5a-b. As can be seen, the $t_{1/2}$ response decreases when the inlet NH$_3$ concentration changes from 300 ppmv to 2000 ppmv. The slope of the response surface is more negatively inclined with increasing inlet NH$_3$ concentration according to the additional term of $X_1^2$ in the quadratic model. The high NH$_3$ concentration generated more (NH$_4$)$_2$SO$_4$ 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$_2$SO$_4$ concentration on the rubber wood biochar surface, $t_{1/2}$ also increased because the higher H$_2$SO$_4$ concentration on RWB surface increased the amount of H$_2$SO$_4$ 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 generating of (NH$_4$)$_2$SO$_4$. The elliptical contour plot shows that the interaction term of $X_1X_2$, which indicates the higher H$_2$SO$_4$ 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$_2$SO$_4$ concentration.

Figure 5c-d depicts the 3D plot and its corresponding contour plot to show the effects of H$_2$SO$_4$ 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$_2$SO$_4$ concentration and 2 l/min waste air flow rate which is in accordance with the model. Increasing the H$_2$SO$_4$ concentration, from 40 to 80 %, increased the $t_{1/2}$. It is very clear that H$_2$SO$_4$ 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$_2$SO$_4$ on the RWB surface was shortened, thus crystals from the reaction between NH$_3$ in the waste air and H$_2$SO$_4$ 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$_2$SO$_4$ concentration at 60%, is shown in the 3D surface plot and its corresponding contour plot in Figure 5e and Figure 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 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 highly amount of NH$_3$ to react with H$_2$SO$_4$ on the surface, (NH$_4$)$_2$SO$_4$ 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.

Figure 5.

3.4 Process optimization using response surface methodology (RSM)

The optimum condition of NH$_3$ adsorption system was obtained using numerical optimization feature of the Design-Expert 8.0.6 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 workplaces (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, similar testing procedure was also applied on activated carbon commercial grade (AC; CGC – 11A in granular form with surface area of 1000-1100 m$^2$/g, purchased from Qualitech Supply Ltd., Part., Songkhla, Thailand) Moreover, AC had been impregnated with H$_2$SO$_4$ 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.

**Figure 6.**

From Figure 6, in comparing the NH$_3$ breakthrough curves of no-impregnation adsorbents (AC and RWB) and sulphuric acidic adsorbents (ACs and RWBs), it is obvious that NH$_3$ adsorption time of acidic adsorbents were much greater, and hence
H$_2$SO$_4$ 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 3 times much 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 integration of breakthrough curves (Rodrigues et al., 2007). Comparison with those of some other adsorbents reported in 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 condition.

Table 6

Table 6 details a literature review comparing some selective adsorbents that had 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 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 (RWBs) was investigated to maximize the symmetric adsorption time ($t_{1/2}$) 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$_2$SO$_4$ concentration, and waste air flow rate, employing response surface methodology (RSM) with central composite design (CCD). The multiple correlation coefficient of determination $R^2$ obtained was 0.9137, inferring that the actual data fitted quite well with the predicted data applying the quadratic model. Regression analysis, ANOVA, and response surface plots were conducted using the Design Expert Software 8.0.6 trial version 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$_2$SO$_4$ 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$_2$SO$_4$ is (NH$_4$)$_2$SO$_4$ crystals which can be used as nitrogen fertilizer for plantation.

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The authors would like to express gratitude to the grants for PhD students provided by the Prince of Songkla University (PSU) to travel overseas to further their thesis researches in foreign countries. We would like to thank also the PSU Graduate School for her financial supports exercised under the Songklanakarin Graduate Studies
Grant. Sincere appreciations are extended too to the PSU Department of Chemical Engineering, Faculty of Engineering in facilitating equipment and laboratory supports.

References


Pollution Control Department, 2005. The methods for pollution prevention and reduction from rubber latex industry, first ed. Ministry of Natural Resources and Environment, Thailand.


FIGURE CAPTIONS

Figure 1. Schematic diagram of NH₃ contaminated waste air generation and treatment system.

Figure 2. Correlation between operating line and breakthrough curve for symmetric adsorption time (t½) determination in NH₃ adsorption system by biochar adsorbent.

Figure 3. SEM photographs (500 x) of RWBs at before (a) and after (b) for NH₃ adsorption in continuous waste air flow adsorption system.

Figure 4. Plot of predicted response vs. actual value for t½ response from reduced surface quadratic model.

Figure 5. 3D surface and contour plotted for combined effect of a,b) inlet NH₃ concentration and H₂SO₄ concentration of 3.5 l/min; c,d) H₂SO₄ concentration and waste air flow rate for 1150 ppmv NH₃; e,f) NH₃ concentration and waste air flow rate under 60% H₂SO₄; on t½ in the NH₃ adsorption system.

Figure 6. Breakthrough curve of NH₃ adsorption from waste air for comparison study between AC and RWB (without acid impregnation) and ACs and RWBs (with sulfuric acid impregnation)
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TABLE CAPTIONS

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

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

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

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<table>
<thead>
<tr>
<th>Coded value</th>
<th>Level of variable</th>
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<tbody>
<tr>
<td>-α</td>
<td>$X_{\text{min}}$</td>
</tr>
<tr>
<td>-1</td>
<td>$[(X_{\text{max}}+X_{\text{min}})/2] - [(X_{\text{max}} - X_{\text{min}})/\beta]$</td>
</tr>
<tr>
<td>0</td>
<td>$(X_{\text{max}}+X_{\text{min}})/2$</td>
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<tr>
<td>+1</td>
<td>$[(X_{\text{max}}+X_{\text{min}})/2] + [(X_{\text{max}} - X_{\text{min}})/\beta]$</td>
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<tr>
<td>+α</td>
<td>$X_{\text{max}}$</td>
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</table>

Where $X_{\text{max}}$ and $X_{\text{min}}$ are maximum and minimum values of $X$, respectively; $\beta$ 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.

<table>
<thead>
<tr>
<th>Independent Variables</th>
<th>Symbol</th>
<th>Coded variable levels</th>
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<tr>
<td></td>
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<tr>
<td>NH\textsubscript{3} inlet concentration (ppmv)</td>
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<tr>
<td>H\textsubscript{2}SO\textsubscript{4} concentration (%)</td>
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<tr>
<td>Waste air flow rate (l/min)</td>
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Table 3. Central composite design consisting of experiments for the study of experimental factors in coded and actual values with responses from experimental results.

<table>
<thead>
<tr>
<th>Standard run no.</th>
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<th>Response values</th>
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<td>X2</td>
<td>X3</td>
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Table 4. ANOVA table (partial sum of squares) for reduce quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F-value</th>
<th>Prob &gt; F</th>
<th>Remarks</th>
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<td>9532.82</td>
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<td>10.45</td>
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</tbody>
</table>

* DF= Degree of freedom  
* C.V.= Coefficient of variation  
* PRESS= Predicted residual sum of squares
Table 5. Optimum condition and model validation of NH$_3$ adsorption system using acidic rubber wood biochar adsorbent.

<table>
<thead>
<tr>
<th>NH$_3$ conc. (ppmv) ($X_1$)</th>
<th>H$_2$SO$_4$ conc. (%) ($X_2$)</th>
<th>Flow rate (l/min) ($X_3$)</th>
<th>Symmetric adsorption time, $t_{1/2}$ (min)</th>
<th>Predicted</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>72</td>
<td>2.1</td>
<td></td>
<td>219</td>
<td>220</td>
</tr>
</tbody>
</table>
Table 6. Comparison of NH$_3$ adsorption capacity of various adsorbents reported in literatures.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural clinoptilolite</td>
<td>12.70</td>
<td>Ciahotný et al. (2006)</td>
</tr>
<tr>
<td>Modified clinoptilolite impregnated with acid</td>
<td>27.60-31.50</td>
<td>Ciahotný et al. (2006)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.60-1.80</td>
<td>Rodrigues et al. (2007)</td>
</tr>
<tr>
<td>Activated carbon impregnated with nitric acid</td>
<td>41.65</td>
<td>Huang et al. (2008)</td>
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<td>Activated carbon impregnated with sulfuric acid</td>
<td>50.00</td>
<td>Liang-hsing et al. (2006)</td>
</tr>
<tr>
<td>Carbonaceous adsorbents from sewage sludge-based</td>
<td>18.7-20.6</td>
<td>Canals-Batlle et al. (2008)</td>
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<tr>
<td>Rubber wood biochar impregnated with sulfuric acid</td>
<td>46.35</td>
<td>This work</td>
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</table>