Optimizing Ammonia Adsorption Using Activated Carbon from Tamarind Pulp

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Ammonia is an essential waste from fish and shrimp which has an effect on fish and shrimp transportation for export. This study aimed to remove ammonia by Activated Carbon adsorption. The activated carbon was prepared from Tamarind pulp using different methods (NaOH, H2SO4, the hydrothermal technique and activated by H2SO4 and H2SO4 hydrothermal followed by NaOH). The Activated Carbon was characterized by and Iodine number and Fourier Transform Infrared Spectroscopy (FT-IR). The results showed that the iodine number of activated carbon prepared by the hydrothermal technique and activated by H2SO4 have the highest surface area and porosity at 537 mg/g, and the functional group on activated carbon surface is carbonyl and sulfonyl group. For ammonia adsorption, the experiments were designed by Box-Behnken design at 3 factors 3 levels including Contact time (10, 95 and 180 min), Dosage of activated carbon (0.5, 1.25 and 2.0 g) and pH of the solution (2, 6.5 and 11). The concentration of ammonia was determined by UV-Visible spectrophotometer. The result showed that the main effects and the interaction effects were found significant effect on ammonia adsorption at confidence level of 95%. However, the interaction effects between contact time and activated carbon dosage was insignificant. Finally, the optimized results suggested that 48.32 ± 0.82% of ammonia concentration could be removed by activated carbon from tamarind pulp under the following conditions: pH of 11, a contact time of 95 min, and activated carbon dosage of 2 g/100 mL. The results are believed to be of importance to fish and shrimp transportation for reduced ammonia and other similar applications.

Key Words
Activated Carbon, Tamarind pulp, Hydrothermal, Chemical activation, Ammonia adsorption

1. Introduction

Tamarind (Tamarind indica L.) can be used for a variety of benefits and there also many vitamins and organic acids. In Thailand, Tamarind is processed into various products which is the use of tamarind meat for production. In order to reduce the amount of waste in the production process and increase the value of the tamarind granary, activated carbon is one of the options to increase the value of the pulp.

Activated carbon, known as activated charcoal, is a form of carbon that have small pores with a very large internal surface area that can produced from carbonaceous source materials. Also can increase the ability of the adsorption, which is physical activation and chemical activation, many researchers have studied to increase surface area and functional groups on the surface of activated carbon to maximize the adsorption efficiency and found that the hydrothermal process can increase the surface area of the activated carbon and acid-base activation can increase the number of functional groups on the surface of activated carbon.

Ammonia is found in the environment, especially in water. It is excreted by plants, animals and produced as a result of the decomposition of organisms and sewage by micro-organisms, the release of fertilizers,
industrial emissions, and volcanic activity. Ammonia in the environment is toxic. Nitrogenous wastes products can become concentrated in aquaculture systems \(^5\) \(^6\). Ammonia is excreted by shrimp, and it can also accumulate in the water because of the decomposition of organic solids, such as excess feed and feces \(^7\). When the ammonia levels get higher, shrimps find it difficult to extract energy from feed. Consequently, they become lethargic and this situation leads to coma stage and death as well. Further, this will affect the quality of the shrimp, including the deterioration of the condition and market share in shrimp exports.

This study aimed to prepare the activated carbon from tamarind pulp with different methods and to optimize the ammonia adsorption by activated carbon prepared from tamarind pulp.

2. Methodology

2.1 Material

Tamarind pulps used in this study were purchased from Pinpetch, Ltd. (Bangkok). For activation, NaOH (AR grade, Merck KGaA, Germany), H\(_2\)SO\(_4\) (AR grade, Labscan Limited, Thailand).

2.2 Proximate analysis of Tamarind pulp

Proximate analysis is formally defined by a group of ASTM test methods and is an assay of the moisture, ash, volatile matter, and fixed carbon content of a sample. The moisture content is determined under ASTM-D373-00 standard methods by the mass loss that a tamarind pulp undergoes after it has been heated to 100 °C for 1 hour in the crucible.

The ash content is determined under ASTM-D2867-70 standard methods by placed the tamarind pulp in the crucible, then heated to 650 °C for 1 hour. After that, cooled down in desiccator then weight the sample before and after.

The volatile matter content of tamarind pulp corresponds to ASTM-D5832-98 by heated crucible to 950 °C for 30 min. Then placed 1 g of Tamarind pulp sample into the crucible and reheated.

For carbon content can be determined by the following equation:

\[
\%\text{Fixed Carbon} = 100 - (\%\text{Moisture} + \%\text{Ash} + \%\text{Volatile Matters}) \quad (I)
\]

2.3 Preparation of activated carbon

The biochar was prepared by dried Tamarind pulps were carbonized at 400 °C for 2 hours (10 °C/min), then the activated carbon was activated by different activation methods such as Activated by NaOH, H\(_2\)SO\(_4\), hydrothermal followed by H\(_2\)SO\(_4\) and H\(_2\)SO\(_4\) hydrothermal followed by NaOH. After activated by following methods, the biochar was carbonized at 500 °C for 1 hour (10 °C/min).

2.4 Characterizations

The activated carbon was characterized by Iodine number method (ASTM-D4607-94). Functional groups of activated carbon were analyzed by using Fourier transform infrared spectroscopy (FT-IR). The spectra were recorded in the range 750-4000 cm\(^{-1}\).

2.5 Ammonia adsorption

2.5.1 Experimental design

The experimental was designed by Box-Behnken Design at three-factor (X1: Contact time, X2: Carbon dosage and X3: pH) and three-level (-1, 0, +1) as shown in Table 1. The total numbers of 30 experimental runs were conducted to assess the effects of independent variable on %ammonia removal and can be calculated as shown in the following equation:

\[
q = \left[\frac{(C_0-C)}{C_0}\right] \times 100 \quad (2)
\]

Where \(q\) is %ammonia removal

\(C_0\) is the initial concentration of ammonia

\(C\) is the final concentration of ammonia

2.5.2 Experimental Run

The experiment was following ASTM-D3860-98 by added 100 mL ammonia solution into flask and following added activated carbon into the flask. Placed the flask in incubator shaker at 125 rpm and filtered by membrane filter and collect the filtrate. Add 1 mL of Nessler's solution into the filtrate and analyze by UV-Visible Spectrophotometer at 425 nm, the total ammonia was calculated by the following equation:

\[
\text{Total Ammonia, mg/L} = \left[\frac{\text{Ammonia nitrogen (mg)}}{1000}\right] \times \text{Volume of sample (mL)} \quad (3)
\]

3. Results and Discussion

3.1 Proximate Analysis

From the result of proximate analysis in Table 2 was shown that in 1 g of tamarind pulp has 96.94% of fixed carbon and 3.06% is moisture, ash, and volatile matter. Thus, tamarind pulp is suitable for preparing the activated carbon.

| Table 1 The Box-Behnken Design of ammonia removal |
|-----------------------------------------------|
| Factor | Level |
|--------|-------|
| X1: Contact time (min) | 10 | 95 | 180 |
| X2: Carbon Dosage (g/100 mL) | 0.5 | 1.25 | 2 |
| X3: pH | 2 | 6.5 | 11 |
3.2 Activation of Biochar

In Table 3, the iodine number of activated carbons can show the surface area of adsorption of activated carbon prepared of various methods. The results showed that activated carbon treated by H$_2$SO$_4$ can increase surface area better than activated NaOH, because H$_2$SO$_4$ is highly corrosive allowing to make a high surface area $^8)$. Hydrothermal is the physical activation which can cause the physical change of the biochar and increase the adsorption performance $^9)$, when combine with the chemical activation can increase the adsorption efficiency. The activated carbon treated by hydrothermal followed by H$_2$SO$_4$ and activated carbon treated by H$_2$SO$_4$ hydrothermal followed by NaOH have a similar result is 537 and 540 mg/g, respectively. In case of using H$_2$SO$_4$ hydrothermal is dangerous cause of high temperature acid. Thus, activated carbon treated by hydrothermal followed by H$_2$SO$_4$ has been choosing to prepare activated carbon from tamarind pulp for ammonia adsorption. The morphology of the activated carbon has been investigated.

3.3 The functional group of activated carbon

Fig. 1 showed the Functional groups of activated carbon treated by hydrothermal followed by H$_2$SO$_4$, investigated by using FT-IR spectra analysis which the x-axis represents the intensity of infrared spectra and the y-axis represents the amount of infrared light transmitted by the material being analyzed. The bands at 1125 and 1650 cm$^{-1}$ show the stretching bond of Sulfonyl (SO$_2$) and Carbonyl (C=O), respectively. The result has showed that this treatment can increase the oxygen-containing functional group on activated carbon surface which is the important functional group that used to adsorbing ammonia $^{10)}$.

Table 2 The result of proximate analysis

| Parameter             | Tamarind pulp |
|-----------------------|---------------|
| Moisture (wt. %)      | 0.14          |
| Ash (wt. %)           | 1.41          |
| Volatile Matter (wt. %) | 1.51      |
| Fixed Carbon (wt. %)  | 96.94         |

Table 3 Iodine number of activated carbons

| Samples                              | Iodine Number (mg/g) |
|--------------------------------------|-----------------------|
| Treated by NaOH                      | 340.12                |
| Treated by H$_2$SO$_4$                | 502.69                |
| Treated by hydrothermal followed by H$_2$SO$_4$ | 537          |
| Treated by H$_2$SO$_4$, hydrothermal followed by NaOH | 540          |

3.4 Response surface methodology and optimization

The result of ammonia removal of activated carbon prepared by tamarind pulp using hydrothermal followed by H$_2$SO$_4$, which all conditions were designed by Box-Behnken technique, which give %Ammonia removal in the results between 0.00 to 46.24%, as in Table 4. The following regression equation, with a R$^2$ value of 90.44%, was obtained as in Table 5:

\[
\%\text{NH}_3\text{ removal} = 30.09 + 0.0480X_1 - 34.54X_2 - 5.64X_3 \\
- 0.000688X_1X_1 + 8.86X_2X_2 + 0.2861X_3X_3 \\
+ 0.01689X_1X_3 + 2.567X_2X_3
\]

Where $X_1 = \text{Time (min)}$

$X_2 = \text{Dosage (g/100 mL)}$

$X_3 = \text{pH}$

The predicted results can be calculated by Eq. (2). Then, the internal standard residual was applied to check how well the model satisfies the assumption of the analysis of variance (ANOVA).

As in Fig. 2, a normal probability plot of standard residual from least-square-fit plot showed the data along a straight line. The frequency of residual in normal distributions was shown in the histogram. The residual versus the fitted value showed randomly scattered around the zero line. Thus, it can be concluded that the information obtained from this experiment is accurate and reliable. In order to establish the relationship between investigated factors and Ammonia removal percentage, the data were graphically displayed using Pareto charts (Fig. 3). A Pareto chart is a bar graph which shows the absolute values of the standardized effects where individual values are represented in descending order by bars, and the reference line that used to indicate which effects are statistically significant which found that the most important effect was pH and there is one factor that has no effect on ammonia removal is the interaction between Time (min) and Dosage (g/100 mL), that is, P-Value less than 0.05.
Table 4  Box–Behnken design and the response for the yield of %removal

| Runs | Time (min) | Dosage (g/100mL) | pH    | %Removal |
|------|------------|------------------|-------|----------|
| 1    | 95         | 1.25             | 6.5   | 5.75     |
| 2    | 180        | 2                | 6.5   | 13.78    |
| 3    | 10         | 1.25             | 11    | 10.94    |
| 4    | 95         | 0.5              | 11    | 19.33    |
| 5    | 180        | 1.25             | 11    | 23.04    |
| 6    | 95         | 1.25             | 6.5   | 7.73     |
| 7    | 180        | 1.25             | 2     | 0.00     |
| 8    | 180        | 2                | 6.5   | 11.56    |
| 9    | 95         | 1.25             | 6.5   | 6.37     |
| 10   | 10         | 2                | 6.5   | 4.89     |
| 11   | 95         | 2                | 2     | 0.00     |
| 12   | 10         | 2                | 6.5   | 4.02     |
| 13   | 10         | 0.5              | 6.5   | 2.30     |
| 14   | 10         | 1.25             | 2     | 3.40     |
| 15   | 95         | 0.5              | 11    | 15.15    |
| 16   | 95         | 2                | 2     | 4.15     |
| 17   | 95         | 1.25             | 6.5   | 3.22     |
| 18   | 180        | 0.5              | 6.5   | 7.04     |
| 19   | 180        | 1.25             | 2     | 0.00     |
| 20   | 180        | 0.5              | 6.5   | 9.07     |
| 21   | 95         | 0.5              | 2     | 0.00     |
| 22   | 10         | 1.25             | 2     | 0.00     |
| 23   | 10         | 0.5              | 6.5   | 1.30     |
| 24   | 95         | 1.25             | 6.5   | 1.86     |
| 25   | 95         | 2                | 11    | 46.24    |
| 26   | 95         | 1.25             | 6.5   | 15.45    |
| 27   | 180        | 1.25             | 11    | 34.02    |
| 28   | 95         | 2                | 11    | 45.80    |
| 29   | 10         | 1.25             | 11    | 9.83     |
| 30   | 95         | 0.5              | 2     | 14.86    |

Table 5  Regression coefficients for %removal in activated carbon

| Term                               | Coef  | SE Coef | T-Value | P-Value | VIF   |
|------------------------------------|-------|---------|---------|---------|-------|
| Constant                           | 6.73  | 2.03    | 3.32    | 0.003   |       |
| Time(min)                          | 3.11  | 1.24    | 2.51    | 0.021   | 1.00  |
| Dosage(g/100mL)                    | 3.77  | 1.24    | 3.03    | 0.007   | 1.00  |
| pH                                 | 13.01 | 1.24    | 10.47   | 0.000   | 1.00  |
| Time(min)*Time(min)               | -4.97 | 1.83    | -2.72   | 0.013   | 1.01  |
| Dosage(g/100mL)*Dosage(g/100mL)   | 4.99  | 1.83    | 2.73    | 0.013   | 1.01  |
| pH*pH                              | 5.79  | 1.83    | 3.17    | 0.005   | 1.01  |
| Time(min)*Dosage(g/100mL)         | 0.49  | 1.76    | 0.28    | 0.784   | 1.00  |
| Time(min)*pH                       | 6.46  | 1.76    | 3.68    | 0.001   | 1.00  |
| Dosage(g/100mL)*pH                | 8.66  | 1.76    | 4.93    | 0.000   | 1.00  |

S = 4.97014  R² = 90.44%  R²(adj) = 86.14%
Fig. 4 shows the main effect plot indicating that the increase of Contact time can increase the ammonia removal efficiency in the range of 10-95 min and equilibrium after 95 min because of the available active site in the initial of adsorption. High activated carbon dosage promoted an increase in the ammonia removal efficiency, probably due to the more available of surface area and active site and the change of pH of the solution from 2.0 to 11.0 exhibited a positive influence resulting in an increase the adsorption effectively.

Fig. 5 shows the effects of interaction for %ammonia removal. When the contact time and dosage increased, higher contact time and pH, the amount of adsorbents and pH increased, resulting in a higher percentage of ammonia
Finally, the condition was optimized for the maximum %ammonia removal. The results showed the optimum condition was found at the contact time of 180 min, dosage of 2 g/100 mL of sample and pH of 11.0 can remove ammonia in the sample solution 49.05%, the optimum condition was shown in Table 6.

The prediction of model was resulting in average of ammonia removal 48.32% or 2.56 mg/g. the experimental value closely agrees with the predicted values, showing that RSM was an effective for estimating the optimum condition. The data was shown in Table 7.

4. Conclusion

In this study, the activated carbon treated by hydrothermal following by H$_2$SO$_4$, prepared from tamarind pulp could be the most suitable methods from 4 methods in adsorbing ammonia, the functional group was investigated by FT-IR and shown the oxygen-containing group such as Sulfonyl (SO$_2$) and Carbonyl (C=O) which is important functional group in ammonia adsorption. Thus, Box-Behnken design was applied to investigate the important parameters to maximize the ammonia removal at 3 factors (Contact time, Dosage, pH) at 3 levels.

It was seen from the results that the pH of the sample were shown the most effect on the ammonia removal significantly. The optimum conditions was found at the contact time of 180 min, dosage of 2 g/100 mL of sample and pH of 11.0 can predict the ammonia removal of 49.05%. Thus, this optimum condition can be used at the actual situation and use. Tamarind pulp, which is highly available in food industry, is a potential alternative source for preparing activated carbon.

Table 6  The optimum condition for ammonia removal

| Variable         | Setting |
|------------------|---------|
| Time (min)       | 180     |
| Dosage (g/100mL) | 2       |
| pH               | 11      |
| %Removal         | 49.05   |

Table 7  Comparison of predicted and experimental values for ammonia removal

| Run No. | 1     | 2     | 3     | Average |
|---------|-------|-------|-------|---------|
| %Removal| 49.06 | 47.43 | 48.47 | 48.32   |

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