Fruit waste adsorbent for ammonia nitrogen removal from synthetic solution: Isotherms and kinetics

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Abstract. In this study, four types of watermelon rind (WR) adsorbents; fresh WR, modified WR with sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulphuric acid (H₂SO₄) were used as a potential low-cost adsorbent to remove NH₃-N from solution. The adsorption data were fitted with the adsorption isotherm and kinetic models to predict the mechanisms and kinetic characteristics of the adsorption process. The equilibrium data agreed well with Langmuir isotherm model with highest correlation (R²=1.00). As for kinetic modelling, the adsorption process follows pseudo-second order for all four types of adsorbents which has R² value of 1.0 and calculated adsorption capacity, Qₑ of 1.2148mg/g. The calculated Qₑ for pseudo-second order has the smallest difference with the experimental Qₑ and thus suggest that this adsorption process is mainly governed by chemical process involving cations sharing or exchange between WR adsorbent and NH₃-N in the solution.

1. Introduction
Excess ammonia nitrogen (NH₃-N) discharged into water source can cause environmental problems including eutrophication, depletion of dissolved oxygen and toxicity to fish and other aquatic organisms[1]. Thus, prevention of nitrogen pollution with ammonium removal from waterways is important. Commonly, NH₃-N removal is achieved by ozonation[2], air stripping[3], chemical precipitation[4] and adsorption[5]. Adsorption is one of the best NH₃-N removal methods and it is economically feasible and environmental friendly[6]. Great efforts have been made to identify new low-cost adsorbent and fruit waste is one of promising material as an adsorbent. Fruit crops use around 375,000 hectares (5.4%) of land in Malaysia[7] and has total production of 1.8 million metric tons[8] thus leaving behind a large quantities of wastes resulting from the production and food consumption chain. Fruit wastes are unlimited, abundance and cheap[9] thus makes it convenient for experimental purposes. Disposal of fruit waste adsorbent after adsorption process can be accomplished either by composting or incineration[10].

In this study, watermelon waste was utilized as fruit waste adsorbent in NH₃-N adsorption. Watermelon biomass can be categorised into three main components; the flesh, seed and rind. The flesh constitutes approximately 68% of the total weight, the rind approximately 30%, and the seeds approximately 2%[11]. Watermelon rind (WR) was the only part used for this research. The skin of

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fully ripened watermelon contain approximately 20% cellulose, 23% hemicellulose, 10% lignin, 13% pectin, 7 mg/g silica and 12% silica free minerals[12]. Previously, it has been reported that the adsorption capacity of solid adsorbent can be increased by chemical modification or pre-treatment method [13-16]. A comparison of adsorption capacity between unmodified and chemically modified adsorbents with sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulphuric acid (H_2SO_4) was reported in this study.

Previous research proves that WR adsorbent can removed variety of pollutant from wastewater such as heavy metals [17] and dyes [18]. However, available information on the NH_3-N adsorption by watermelon rind still limited. The main purpose of this study is to determine the isotherms and kinetics adsorption in order to obtain an insight into the equilibrium characteristics of ammonia adsorption by watermelon rind. The adsorption isotherm and kinetic modelling were studied by fitting the equilibrium data into different types of isotherm (Langmuir, Freundlich, Temkin) and kinetic (Pseudo-first order, pseudo-second order and Intra-particle) models.

2. Materials and Methods

Watermelon rinds were collected from Kota Kinabalu area. The rinds were washed thoroughly with tap water and rinsed with distilled water to remove any impurities. Next, the WR samples were cut into small pieces (around 1 to 2 mm^2) and dried in an oven at 40°C for 48 hours to a constant weight[19]. For chemically modified adsorbent, the WR was soaked in 1 L NaOH solution (20mmol/L), 1 L KOH solution (20mmol/L) and 1 L H_2SO_4 solution (20mmol/L) respectively for 24 h[13]. The watermelon rind was then dried further in an oven at 40°C for 48 hours.

Synthetic ammonium solutions were used throughout the adsorption tests. First, ammonium chloride salt (NH_4Cl) with calculated weight and distilled water were used for the preparation of a stock NH_3-N solution of 50 mg/L. Then, the experimental solutions at the desired ammonium concentrations were prepared by diluting the stock solution with distilled water. The initial pH was adjusted to 7.0 using dilute solutions of NaOH (0.1 N) throughout the experiments [19].

Batch experiments consisted in analysing the zeta potential and effect of contact time and mass of adsorbent on the NH_3-N adsorption by all four types of WR adsorbent. All the samples were adjusted to the optimum pH prior to the addition of the adsorbent. Sample solutions were withdrawn at certain intervals in order to determine the residual concentration by using UV-vis spectrophotometer with HACH Spectrophotometer DR2010 brand at the maximum wavelength of 425 nm. Hence, the amount of ammonia nitrogen adsorbed at equilibrium, q_e (mg/g) was calculated as followed:

\[
q_e = \frac{(C_0-C_e)V}{W}
\]  

where C_0 and C_e (mg/L) are the liquid-phase concentrations of initial adsorbate and equilibrium, respectively. V is the volume of the solution (L) and W is the weight of the adsorbent (g).

2.1 Adsorption isotherm and kinetics studies

The amount of adsorbed solute onto the solid phase (mg/g) versus the solute concentration in the aqueous phase (mg/L) at equilibrium that called sorption isotherm[20]. This was carried out by fitting the equilibrium data to the Langmuir[21], Freundlich[22] and Temkin[23] isotherms. In order to predict the mechanism involved during the present adsorption process and the potential rate controlling steps such as mass transport, pore diffusion and chemical reaction processes, three kinetic models were used to fit the experimental data, namely, pseudo-first-order[24], pseudo-second-order[25] and intra-particle diffusion[26] models for varied type of adsorbents.
3.0 Result and Discussions

3.1. Adsorption isotherm modelling

Figure 1 shows the Langmuir isotherm for four different types of adsorbent. The Langmuir isotherm model exhibited an excellent fit to the adsorption equilibrium data with highest $R^2$ value of 1.00. The best fit of adsorption data in Langmuir isotherm model confirms the monolayer adsorption of NH$_3$-N onto WR adsorbents. Fresh WR adsorbent shows the highest maximum monolayer adsorption capacity, $Q_m$ of 1.2192 mg/g and followed by modified WR with KOH ($Q_m$=1.2051 mg/g), modified WR with H$_2$SO$_4$ ($Q_m$=1.1892 mg/g) and lastly modified WR with NaOH ($Q_m$=1.1885 mg/g) as shown in Table 1. Several studies on the adsorption of NH$_4^+$ ions onto different types of fruit waste adsorbents shows different maximum monolayer adsorption capacity; strawberry leaves ($Q_m$=6.71 mg/g) and strawberry stems ($Q_m$= 4.62 mg/g)[1], partly decomposed empty fruit bunch ($Q_m$=0.821mg/g)[20]. Different adsorption capacities of various adsorbent are due to the properties of each adsorbent (structure, surface area) and different experimental condition (initial concentration, mass of adsorbent).

For Freundlich isotherm model, the linear regression coefficient, $R^2$ of NH$_3$-N adsorption on the adsorbents ranges from 0.9985-0.9997. The values for Freundlich isotherm constant, $n$ positioned within -38.6 to -92.6 as shown in Table 1. This values showed unfavourable adsorption process as the values does not satisfies the condition $|1|< n<|10|$ [18]. As for Temkin isotherm graph, the constant $B$ is related to the heat of adsorption. Negative values of $B$ Temkin constant were obtained for all four types of adsorbents ranges from -0.0316 to -0.0258kJ/mol. The $R^2$ values for all four adsorbents positioned within of 0.9985-0.9997 as shown in Table 1.

![Figure 1. Langmuir Isotherm](image-url)
Table 1. Isotherm parameters

| Isotherm      | Adsorbent                              | Fresh watermelon rind | Modified watermelon rind with NaOH | Modified watermelon rind with KOH | Modified watermelon rind with H₂SO₄ |
|--------------|----------------------------------------|-----------------------|-----------------------------------|----------------------------------|------------------------------------|
| Langmuir     | Qₑ (mg/g)                              | 1.2192                | 1.1885                            | 1.2051                           | 1.1892                            |
|              | R²                                      | 1.00                  | 1.00                              | 1.00                             | 1.00                               |
| Freundlich   | Kf ((mg/g)(dm³/mg)¹/n)                  | 92.6                  | 41.7                              | 47.4                             | 38.6                               |
|              | n                                       | 1.2268                | 1.2210                            | 1.2238                           | 1.2237                            |
|              | R²                                      | 0.9988                | 0.9995                            | 0.9997                           | 0.9985                            |
| Temkin       | B (kJ/mol)                             | -0.0134               | -0.0295                           | -0.0258                          | -0.0316                           |
|              | R²                                      | 0.9988                | 0.9995                            | 0.9997                           | 0.9985                            |

3.2. Adsorption Kinetic Modelling

Kinetic modelling is used to investigate the adsorption mechanism and rate controlling step. The concentration of the solution was measured by taking the adsorbent-adsorbate solution at present time intervals as shown in equation 2 below:

\[ q_t = \frac{(C_0-C_t)V}{W} \]  

(2)

where \( C_0 \) and \( C_t \) (mg/L) are the liquid –phase concentrations of adsorbate at initial and at any time, \( t \), respectively. \( V \) is the volume of solution and \( W \) is the mass of adsorbent used [27]. Figure 2 shows the linearized plot of pseudo-second order for NH₃-N adsorption onto fresh WR, modified WR with NaOH, KOH and H₂SO₄. The correlation coefficients and the other parameters calculated from the all three kinetic models are given in Table 2.

![Figure 2. Pseudo-Second order](image-url)
It was observed that the pseudo first-order kinetic model did not adequately fit the experimental values ($R^2 < 0.60$). Besides that, the difference between experimental and calculated equilibrium adsorption capacity is very high as shown in Table 2. In contrast, the pseudo-second order rate equation for sorption of ammonium onto adsorbents agreed well with the data ($R^2=1.00$). The calculated equilibrium sorption capacity, $Q_{e,cal}$ for the pseudo second-order was 1.2148 mg/g and it is close to the experimental data values range from 1.2151 to 1.2332 mg/g. This explained that the adsorption process is mainly governed by sharing or exchange of cations between the adsorbent and ammonium ions in the solution [28]. As for intra-particle diffusion model, the experimental data were poorly fitted to intra-particle diffusion model with low $R^2$ values ($R^2 < 0.60$) compared to pseudo-first and pseudo-second order.

### Table 2. Kinetic rate constants

| Kinetic Models | Types of adsorbents | Fresh watermelon | Modified NaOH | Modified KOH | Modified H$_2$SO$_4$ |
|----------------|---------------------|------------------|---------------|--------------|----------------------|
| Experimental $Q_e$ | 1.2332 | 1.2151 | 1.2237 | 1.2165 |
| Pseudo-first-order model | $k_1$ (min$^{-1}$) | 0 | -0.0242 | 0.1740 | -0.1019 |
| Calculated $Q_{e,cal}$ (mg g$^{-1}$) | 0 | 0.3022 | 0.0004 | 0.2871 |
| $R^2$ | 0 | 0.0096 | 0.5602 | 0.1905 |
| Pseudo-second-order model | $k_2$ (min$^{-1}$) | -616.02 | -616.02 | -616.02 | -616.02 |
| Calculated $Q_{e,cal}$ (mg g$^{-1}$) | 1.2148 | 1.2148 | 1.2148 | 1.2148 |
| $R^2$ | 1.000 | 1.000 | 1.000 | 1.000 |
| Intra-particle diffusion | $k_p$ (mg g$^{-1}$ min$^{-1/2}$) | 0.1950 | 0.1921 | 0.1935 | 0.1923 |
| $R^2$ | 0.1896 | 0.2545 | 0.2019 | 0.5534 |

**4. Conclusion**

The adsorption data of NH$_3$-N onto watermelon rind adsorbents has been fitted with isotherm and kinetic models. The experimental data correlated well with Langmuir isotherm model with highest $R^2$ value of 1.00 and thus theoretically suggest that the NH$_3$-N is removed by monolayer adsorption process. The experimental data fitted well with pseudo-second model with $R^2$ value of 1.00 and has the closest value of experimental and theoretically calculated $Q_e$ of 1.2192 mg/g. Thus, confirm the adsorption process of NH$_4^+$ ions onto adsorbent is governed by sharing or exchange of cat-ions. The present study shows that the WR have great potential to be used as adsorbent for the NH$_3$-N removal.

**5. References**

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