Kinetic Study of Ammonia Removal using Activated Rice Husk

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Abstract. Ammonia pollution causes eutrophication and algal bloom, which eventually disrupts the marine ecosystem's equilibrium. Efforts have been made to either recover or remove ammoniacal nitrogen from water resources. Electrochemical, precipitation, adsorption, biological and membrane technology have been developed with varying degrees of complexity and arrangement to overcome this problem. To date, adsorption is widely used to remedy water resources as it is cost and energy effective while being simple to operate and maintain. Adsorption kinetic models are important in evaluating the performance of adsorbent and reveals the adsorption mass transfer mechanism. Nevertheless, the kinetic studies reported in the literature was not complete as only a few models were considered. Meanwhile, the statistical parameter to validate the model was commonly depended on R^2 value alone. The objective of this study is to provide a comprehensive kinetic study of ammonia adsorption using activated rice husk, to the readers by investigating the validity of 9 kinetic models in fitting the experimental data. All the models are validated by using R^2, \( \chi^2 \), residual sum of square (SSE) and (mean square error) MSE. Result showed > 0.99 R^2 values and low \( \chi^2 \), SSE, MSE were found for Mixed order, Ritchie’s and Elovich models. This indicates that the ammonia adsorption process was governed by the adsorption at the active sites of the adsorbent and it was mainly driven by the chemisorption.

1. Introduction
Ammonia is part of the normal nitrogen circulation cycle in nature, but in the case of water pollution, an industrial source of ammonia causes excessive water pollution. Eutrophication and algal bloom cause disruptions of the marine ecosystem's equilibrium. Augmented the concentration of ammonia in water has a particularly adverse effect on the development of fish, causing gill damage, hyperplasia and major growth rate reduction [1]. Despite the harmful effects of ammonia as a form of pollutant, it is a common raw material in fertilizer and animal feed manufacturing, as well as being used as a chemical precursor in fibres, plastics, explosives, paper and rubber production. As such, it is common to find various forms of nitrogen pollutants in agricultural, domestic and industrial wastewater [2].

Thus, efforts have been made to either recover or remove ammoniacal nitrogen from water resources. Several examples of ammonia removal or reduction include, but not limited to, electrochemical, precipitation, adsorption, biological and membrane technology have been developed with varying degrees of complexity and arrangement [3]. At present, adsorption is an attractive method to remedy water resources as it is cost and energy effective while being simple to operate and maintain. Common adsorbent materials such as carbon, clay, activated sludges, polymer and zeolite...
have been produced to extract pollutants from wastewater. A good adsorbent has several defining characteristics such as having a high surface area and pore volume and high thermal stability, making them ideal for extracting organic and inorganic contaminants from wastewater and air [4].

Rice husk (RH) is one of the popular adsorbents for wastewater treatment use due to its availability and low cost. Effort has been done to produce biochar from RH via pyrolysis to increase the negatively charged surface area for ammonia removal [5]. The result showed that biochar enhanced the ammonia adsorption capacity by 1.04 times compared to the untreated sample. Similarly, the nitrate removal also increased to 22.12 mgN/g, which was 3.89 times higher than the untreated sample. Besides, the use of RH in removing pollutants such as dyes, phenol, lead and fluoride, were also investigated by the researchers, as showed in Table 1. It is notable that that thermal and chemical treatments are commonly used to enhance the adsorptive capacity of RH. Among the chemical treatments, acid treatment is preferred compared to others.

Table 1 also presented that the kinetic model of adsorption is depends on the pollutants, which is also known as adsorbates, and the method used to process RH. For instance, Pseudo Second Order (PSO) described the adsorption of methylene blue (MB) well, as reported by Labaran et al. [6] while Quansah et al. [7] found that Pseudo First Order (PFO) matched the MB adsorption data better than PSO. This may due to different method used to produce RH, which affects the adsorptive properties of the adsorbents. On another hand, crystal violet (CV) fitted PSO better compared to MB as reported by Quansah et al [7] even though the same adsorbent was used for experiment. It indicated the interaction between the adsorbate and adsorbent contributes to a great impact on the adsorption mechanism.

| Method | Pollutants | Best fitted kinetic model | References |
|--------|------------|---------------------------|------------|
| Washed RH was air dried for approximately 10 days | Methylene blue (MB) | PSO, $R^2 = 0.995$ | [6] |
| RH was pyrolyzed at varied temperature (75 – 700°C) and crystal violet (CV) | Methylene blue (MB) and crystal violet (CV) | MB fitted PFO ($R^2 = 0.9848$) while CV fitted PSO ($R^2 = 0.649$) | [7] |
| RH was pyrolyzed at 600°C for 4 h | Phenol | Fick model, $R^2 = 1.0$ | [8] |
| RH was dried at 105°C for 3 days | Malachite Green | PSO, $R^2 = 0.986$ | [9] |
| Pyrolyzed RH was soaked in nitric acid for 1 h | Methylene blue | Weber and Morris intraparticle diffusion, $R^2 = 0.9675$ | [10] |
| Pyrolyzed RH was soaked in hydrochloride acid | Lead | Both PFO and interparticle diffusion models with $R^2 = 0.99$ | [11] |
| RH was soaked in phosphoric acid for 25h and dried at 110°C for 6h | Fluoride | PSO, $R^2 = 0.985$ | [12-13] |
| Pyrolyzed RH was mixed with potassium hydroxide at 750°C for 1h | Phenolic compounds | PSO with $R^2 = 0.999$ | [14] |
| RH was soaked in potassium permanganate and heated at 180°C for 4h | Malachite Green | Elovich, $R^2 = 0.998$ | [15] |
| Isopropanol treated RH was functionalized with iron oxide | Methylene blue | PSO, $R^2 = 0.994$ | [16] |

In the review done by Wang and Guo [17] lately, the physical meaning of kinetic models and the respective mathematical derivations were described. Diffusion models such as Boyd’s external diffusion equation, Mathews and Weber and phenomenological external mass transfer (EMT) models assume that the diffusion of adsorbate in a bounding liquid film around the adsorbent is significant compared to internal diffusion. Ritchie’s equation assumed that adsorption at active sites govern the entire adsorption process. Commonly used models such as PFO and PSO are empirical models that
lack physical meaning but the constant value in the equations is important as it represents how fast the adsorption equilibrium is achieved. This information is important in evaluating the performance of adsorbents, especially in designing the adsorption system.

Kinetic models also provide insights to the engineers on the possible methods to improve the adsorption process, once the determining step in adsorption process was identified by the kinetic models. Thus, it is important to conduct a comprehensive kinetic study for an adsorbent. Some of the kinetic studies reported in the literature was not complete, for example, less than 5 kinetic models were studied by Labaran et al. [6] and Muin [9], which may not able to provide a comprehensive finding to the readers about the adsorption mechanism. Additionally, the use of R2 as the sole statistical parameter to validate a model is deficient.

The objective of this study is to bridge the research gap by investigating alkali treated ARH in ammonia adsorption, which is not extensively studied by the researchers, as showed in Table 1. Sharath et al. [18] produced ARH by using sodium hydroxide, the properties of the ARH were well documented but the kinetic studies on adsorption is not available. 9 models which cover the kinetic models and adsorption mechanisms are studied to evaluate the performance of ARH and reveal the mass transfer mechanism. Lastly, all the models are validated by using R2, χ2, residual sum of square (SSE) and (mean square error) MSE.

2. Materials and Methodology

2.1. Material
Raw rice husk was purchased from a local mill in Selangor, Malaysia. Sodium hydroxide pellets were purchased from Fisher Chemicals.

2.2. Methodology
30 g of raw rice husk was washed with RO water to remove dirt and visible impurities and dried in an oven at 105 °C for 24 h. Once drying is completed, the dried rice husk was placed into a furnace and charred for 1 h at 400 °C. After the charring process, the charred rice husk was left to cool to room temperature. The rice husk was then soaked in 1 M NaOH solution for 24 h to activate it. Then, the NaOH solution was drained off and the activated rice husk (ARH) is dried in the oven for 80 °C for 24 h to remove any moisture. The dried ARH is collected and stored in a desiccator for further use.

1.5 g ARH was dispersed into 200 mL of ~100 ppm ammonia solution. The mixture was stirred at 150 rpm in an incubator shaker at room temperature. Appropriate amounts of sample were collected hourly to measure the adsorption performance of ARH. The concentration of ammonia was measured by using Salicylate Method (Method 8155).

2.3. Kinetic models
Nine kinetic models as listed in Table 2 were selected in this study to provide the readers with a comprehensive adsorption mechanism of ARH on ammonia adsorption. The equations of the respective models and its physical meaning are tabulated in Table 2. Generally, \( q_t \) is defined as the amount of adsorbate adsorbed on adsorbent at time \( t \), while the amount of adsorbate adsorbed on adsorbent at equilibrium state is labelled as \( q_e \) at infinity time (\( q_\infty \)). \( k_1, k_2, k_1', k_2', k_n, R \) are the rate constants of the respective models, \( K_{MBW} \) is the mass transfer co-efficient and \( k_{WSM} \) is the intraparticle diffusion coefficient. For Elovich model, \( a \) is the initial adsorption rate constant while \( b \) is the desorption rate constant. \( n \) is known as the number of active sites on the adsorbent occupied by adsorbate in Ritchie’s equation. \( C_0 \) referred as the initial concentration of adsorbates in the feed, \( m_s \) is amount of adsorbent per unit volume of solution and lastly \( S \) is the outer surface of adsorbent per unit volume.
Table 2. List of kinetic models adopted in this study with the physical meaning [17].

| Kinetic model   | Equation                                      | Physical meaning                                                                 |
|-----------------|-----------------------------------------------|----------------------------------------------------------------------------------|
| PFO             | \( q_t = q_e (1 - e^{-k_1 t}) \)             | Well describe the initial adsorption process, especially for the condition where very high initial concentration of adsorbate is considered. |
| PSO             | \( q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \) | Well describe the final adsorption process, especially for the condition where very low initial concentration of adsorbate is considered. |
| Mixed order (MO)| \( dq_t = k_1 (q_e - q_t) + k_2 (q_e - q_t)^2 \) | For arbitrary stage of adsorption.                                                |
| Pseudo-nth-order (PNO)| \( q_t = q_e (1 - \frac{1}{1 + (n - 1) - q_e^{n-1} k_n t^{1/(n-1)}}) \) | For arbitrary stage of adsorption.                                                |
| Elovich         | \( q_t = \frac{1}{b} \ln(1 + abt) \)        | Extensively applied to chemisorption data.                                        |
| Ritchie’s equation | \( q_t = q_\infty - q_\infty (1 + (n - 1) \propto t)^{\frac{1}{n-1}} \) | Active sites dominated the adsorption process and one adsorbate can occupy more than 1 active site. |
| Boyd’s external diffusion equation | \( q_t = q_\infty (1 - e^{-k_1 t}) \) | Assumes linear concentration gradient for adsorbate diffusion through a bounding liquid film. |
| Matthews and Weber (M&W) | \( q_t = \frac{C_0}{m_s} (1 - e^{-k_M W S t}) \) | Describes external diffusion process.                                             |
| Weber and Moris (W&M) | \( q_t = k_{W&M} t^{0.5} \)             | Describes intraparticle diffusion process.                                        |

2.4. Statistical analysis

The following statistic parameters were used to evaluate the validity of the kinetic models.

\[
R^2 = \frac{\sum(q_{\text{mean}} - q_{\text{cat}})^2}{\sum(q_{\text{cat}} - q_{\text{mean}})^2 + \sum(q_{\text{cat}} - q_{\text{exp}})^2} \tag{1}
\]

\[
\chi^2 = \frac{q_{\text{cat}}}{\sum(q_{\text{exp}} - q_{\text{cat}})^2} \tag{2}
\]

\[
SSE = \sum(q_{\text{exp}} - q_{\text{cat}})^2 \tag{3}
\]

\[
MSE = \frac{1}{N_{\text{exp}}} \sum(q_{\text{exp}} - q_{\text{cat}})^2 \tag{4}
\]

3. Result and Discussion

Figure 1 describes the experimental adsorption capacity of ARH for ammonia removal at different time interval. The predicted adsorption capacities were calculated from 9 different kinetic models, as described in section 2.3. The experimental data showed that the equilibrium capacity of ARH is approximately 3.8 mg/g. This is comparable with the recent study done by Khalil [19], where the capacity of the activated biochar was within 2.9 to 4.5 mg NH\(_4\)/g at temperature 25 to 45°C. The use of sections to divide the text of the paper is optional and left as a decision for the author. Where the author wishes to divide the paper into sections the formatting shown in table 2 should be used.
Figure 1. Experimental and predicted adsorptive capacity of ARH at different time interval.

It is notable that majority of the predicted adsorption capacities showed in Fig.1. are very close to the experimental data, except for the results predicted from M&W model and W&M model. This indicates that external diffusion and internal diffusion proposed by M&W model and W&M model respectively, did not govern the ammonia adsorption process. Nevertheless, it is contrast with the Boyd’s external diffusion equation, as this model showed 0.996916 of $R^2$ value, low SSE, $\chi^2$, MSE and HYBRID values as presented in Table 3. This is because the model showed the similar equation as PFO at the initial stage of adsorption, where the concentration of adsorbate on absorbent is closes to zero [17].

Table 3. Kinetic model constants and validity evaluation

| Kinetic models     | Constants | $R^2$   | SSE  | $\chi^2$ | MSE   |
|--------------------|-----------|---------|------|----------|-------|
| PFO                | $k_1 = 1.8631 \text{ h}^{-1}$ | 0.998146 | 0.019142 | 0.005245 | 0.003828 |
| PSO                | $k_2 = 0.9198 \text{ g.mg}^{-1} \text{ h}^{-1}$ | 0.998395 | 0.016550 | 0.004449 | 0.003310 |
| MO                 | $k_{11} = 0.79470 \text{ h}^{-1}$ | 0.998620 | 0.01423 | 0.00385 | 0.00285 |
|                    | $k_{12} = 0.64624 \text{ g.mg}^{-1} \text{ h}^{-1}$ | | | | |
| PNO                | $k_d = 0.520687 \text{ g}^{1.5} \text{.mg}^{-1.5} \text{ h}^{-1}$ | 0.998202 | 0.018550 | 0.004975 | 0.003710 |
|                    | $n = 2.524527$ | | | | |
| Elovich            | $a = 542.153431 \text{ mg.g}^{-1} \text{h}^{-1}$ | 0.997286 | 0.027941 | 0.007515 | 0.005588 |
|                    | $b = 2.226445 \text{ g.mg}^{-1}$ | | | | |
| Ritchie’s equation | $\alpha = 1.415611 \text{ h}^{-1}$ | 0.994661 | 0.057445 | 0.015298 | 0.011489 |
|                    | $n = 0.753902$ | | | | |
| Boyd’s external    | $R = 1.713319 \text{ h}^{-1}$ | 0.996916 | 0.032894 | 0.008996 | 0.006579 |
| diffusion equation | $k_{\text{M&W}} = 0.104586 \text{ cm. h}^{-1}$ | 0.745566 | 5.139153 | 2.761190 | 1.027831 |
| M&W                | $k_{\text{W&M}} = 2.214533 \text{ mg.g.h}^{1/2}$ | 0.882817 | 1.600617 | 0.581206 | 0.320123 |
Table 3 tabulated the constants obtained from 9 different kinetic models and the respective statistical parameters. Generally, the adsorption data fitted the empirical models, PFO, PSO, MO, PNO and Elovich models well, with $R^2 > 0.99$. Thus, it is difficult to justify which model predicted the data the best based on $R^2$ alone. From the statistical data, PNO exhibited the lowest SSE, $\chi^2$ and MSE values. This indicated that PNO is the best model to fit the ammonia adsorption data. This is because the PNO combined PFO and PSO, which are excel in predicting the initial and final stages of adsorption process [17]. Compare to the work done by Khalil et al [19] on ammonia removal using rice straw, PSO was reported as the best model to describe the kinetic adsorption with $R^2 = 0.98$. This finding may not be conclusive as MO was not included as part of the study.

Ritchie’s equation model was adopted in this study to find out the role of active sites in adsorption. $R^2 > 0.99$ with 0.057445 SSE, 0.015298 $\chi^2$ and 0.011489 MSE indicated that this model fitted the experiment data well, and the ammonia removal process is dominated by the adsorption process in the active sites. High $R^2$ value and low SSE, $\chi^2$ and MSE for Elovich model suggested the chemisorption mechanism at the active sites. Ritchie’s equation also described MB adsorption by using ball-milled biochar encapsulated in calcium-alginate beads with the $R^2$ value of more than 0.99 [20]. It is recommended to further improve the adsorbent by creating more active sites to enhance separation performance. This can be done by surface modification using surfactant [21], organically-modified magadite [22], and wet attrition method [23].

4. Conclusion
ARH produced in this study removed ammonia by adsorption, and the equilibrium adsorptive capacity of ARH was 3.8 mg/g. PNO described the adsorption process well, with $R^2$ value of 0.998202 and low values of SSE (0.018550), $\chi^2$ (0.004975) and MSE (0.003710). Besides, $>0.99$ $R^2$ values with low SSE, MSE and $\chi^2$ were also found in Elovich model and Ritchie’s equation, which confirmed that adsorption at active sites was the rate limiting step in this adsorption process, and it was driven by chemisorption. It is recommended to modify the surface of the adsorbent to increase the number of active sites to further enhance the adsorption process.

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6. References
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