Ammonium adsorption - desorption using rice husk biochar

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Abstract. Rice husk was utilized into biochar by pyrolysis and used as adsorbent for ammonium removal. Rice husk biochar (RHB) was produced at temperature of 350°C, 400°C, 450°C, 500°C, and 550°C. Characteristics of biochar were analyzed by moisture content, ash content, pH Zero Charge and Fourier Transform Infrared (FTIR) Spectroscopy. As the temperature for the pyrolysis increases, the moisture content of RHB decreases while the ash content of RHB increases. From the pH zero charge analysis, the value obtained from analysis is pH 7. The FTIR spectra showed the organic part of RHB with different functional groups such as alkene, alcohol, phenol, ether, ester etc. Based on the result of the characterization test, RHB500 was chosen as the best biochar for the adsorption of ammonium. The equilibrium contact time was 180 minutes and the optimum adsorbent dosage was 0.1g and the optimum concentration of ammonium was 1.2 ppm. For the adsorption-desorption of ammonium, RHB can run up to 5 cycles for biochar regeneration. Adsorption kinetic, pseudo-second-order model is more preferable than pseudo-first-order model because R2 value is 0.9995 which closer to 1.

1. Introduction

Ammonium is a positively charged ion which is formed when ammonia forms a dative covalent bond with a hydrogen ion. Ammonium is a natural component of many foods. Minor amounts of ammonium compounds (< 0.001-3.2%) are also added to foods as acid regulators, stabilizers, flavoring substances, and fermentation aids. Soluble ammonium ions are one of the most common nitrogen compounds that can cause a series of pollution problems to water bodies [1]. Ammonium is released from municipal, industrial, and agricultural practices. A high concentration of ammonium in groundwater is typically associated with contamination by sewage water or with leakage of manure or mineral fertilizer from agricultural activities [2].

Ammonium does not directly harm to human body. However, it may form nitrite ions under oxidative conditions. Nitrite is a toxic component because it disables the enzyme lactase in the blood cells, causing hydrogen-peroxide to realize. As a result, the hemoglobin is oxidized to methemoglobin, which means that the divalent iron in hemoglobin is oxidized to trivalent iron. Due to the harmful of nitrite, a drinking water standard for the concentration of ammonium that set by World Health Organization (WHO) must below than 0.5 mg/l (ppm) (WHO, 2007). Therefore, the removal of ammonium from a water source is very important to ensure a healthy living lifestyle.

While various treatment methods have been developed for the removal of ammonium from the water source, including biological technology such as nitrification-denitrification process, air stripping, and ion exchange.
As discharge limits of various pollutants become more stringent, ion exchange and adsorption become more interesting as possible treatment methods. Nevertheless, physical removal method using low-cost adsorbents is among the most competitive ways because of its performance and cost [3].

In recent years, another adsorbent was used in adsorption processes is natural adsorbent and most researchers have been seeking to find the adsorbents with higher efficiency and lower cost. The commonly used adsorbent for ammonium adsorption is zeolite. However, zeolite is not cost-effective, compared to other adsorbents. For large amount adsorption of ammonium, biochar has been replaced by the zeolite which it is cheaper and easier to synthesis. Biochar mostly used as the natural adsorbent for heavy metal and ions in the waste water treatment. Natural adsorbent such as rice husk biochar is one of the considerable and applicable sorbents due to their low-cost, availabilities and easy applications in the removal of ammonium contaminants from the environment [4].

The objective of this research is to synthesis the adsorbent from rice husk for ammonium adsorption. Besides, the research aims to evaluate the adsorption and desorption study of ammonium by using rice husk biochar. Desorption is cost-saving and reuse the used biochar for next cycle of adsorption.

2. Methodology

2.1. Sample preparation
Rice husk was used as the raw material to produce the biochar. The rice husk was collected from a paddy industry in Perlis. The rice husks were dried at 105°C for 48 hours in electrical oven to reduce the moisture content to convenient the pyrolysis process. The rice husks were processed through pre-treatment which grinding and sieving into 500μm size of sample.

2.2 Pyrolysis process.
Pyrolysis of sample was performed in a muffle furnace. The dried sample of 15 g was fed in the crucible and was properly cover with cap and placed into the muffle furnace. Pyrolysis was conducted at different temperatures of 350, 400, 450, 500, and 550 °C for 1 hour. The heating rate of 20 °C/min was kept constant for each run.

2.3 Biochar characterization.
Biochar characterization was performed in this study in order to choose the best adsorbent for the ammonium adsorption. The characterization of physical and chemical properties of the produced biochar were performed by using method below:

2.3.1 Moisture and Ash Content Analysis. Moisture and ash content of biochar were analyzed by the biochar after the pyrolysis process. The 1g of the biochar was measured and placed into a dried crucible for future heating. The sample was placed in the oven at 105°C for 5 hours. The mass of biochar at initial and final were recorded for the calculation of moisture. For ash content, biochar was heated in a muffle furnace at 750°C under the atmosphere of air for 6 hours. The pyrolyzed samples typically turned to pale gray powder and exhibit no black particles of residual carbon residue.

2.3.2 FTIR (Fourier-transform infrared spectroscopy). FTIR was used to determine the functional group of biochar. The FTIR instrument send infrared radiation of about 10,000 to 100 cm⁻¹ through a sample, with some radiation absorbed and some passed through. The absorbed radiation was converted into rotational and vibrational energy by the sample molecules. With the resulting signal at the detector presents as a spectrum, typically from 4000 cm⁻¹ to 400cm⁻¹, representing a molecular fingerprint of the sample. The infrared peaks were recorded according the study to measure the functional group of biochar.
2.3.3 **pH Zero Point Charge (pH\textsubscript{zpc}).** In order to assess the effect of initial solution pH adsorption, a certain amount of biochar (0.1 g) was added to 0.1 mol/l HNO\textsubscript{3} solution and 0.1 mol/l NaOH. The initial pH of each NaCl solution (before biochar addition) was adjusted to pH 3, 5, 7, 9, and 11. Then all the sample was added with 50 ml of NaCl into a conical flask. The mixture has been shaken at 250 rpm for 24 h to reach equilibrium. The equilibrium pH of each solution was measured, and the point of zero charge (pH\textsubscript{zpc}) of each biochar was obtained from a plot of initial solution pH against equilibrium solution pH [5].

2.4 **Adsorption process.**

There are several parameters that were investigated throughout this research. There was pH of ammonium, adsorbent dosage, contact time and the initial concentration of ammonium. Adsorption experiments were carried out in an incubator at temperature 30\textdegree C, 250 rpm rotation speed with 250 ml shaking flasks containing 50 ml of ammonium solution with biochar.

2.4.1 **Contact time.** The different contact time was carried out to determine the effect of the contact time to the ammonium adsorption of the biochar. 1, 5, 10, 30, 60, 120, 180, 240 and 300 minutes were chosen as the range of contact time. The sample was treated in the incubator shaker at room temperature 30\textdegree C, speed 250 rpm, ammonium initial concentration 1.2 ppm, 0.1 g of adsorbent, and pH 7.

2.4.2 **Adsorbent dosage.** Different dosages of adsorbent have been carried out by adding the adsorbent into the shaking flasks with ammonium solution. Six different adsorbent dosages which were 0.05 g, 0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g were studied for ammonium adsorption at temperature 30\textdegree C with constant pH 7 of ammonium. The solution with ammonium initial concentration 1.2 ppm was agitated in incubator shaker with 250 rpm with optimum contact time which was obtained from analysis of contact time.

2.4.3 **Initial concentration of ammonium.** Different initial concentrations of ammonium were prepared in shaking flasks. The 6 sample with different concentration of ammonium which in 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 ppm were agitated at 250 rpm in incubator shaker with pH 7 of ammonium, optimum adsorbent dosage and the optimum contact time.

2.5 **Desorption process.**

Adsorption was conducted at solid/liquid ratio of 1g/100ml and temperature 30\textdegree C by using optimum contact time, adsorbent dosage and initial concentration of ammonium that have been obtained. It was started with adsorption process first followed by the desorption process. Desorption process was performed by the addition of 1% NaCl solution until a new equilibrium was reached. After the adsorbent obtained, it reused again for the next adsorption process. This adsorption-desorption process was done in 3-5 cycles to determine the reversibility of adsorbent.

2.6 **Kinetic study.**

The investigation of the mechanism of ammonium adsorption on biochar, two kinetic models, pseudo-first-order kinetic model and pseudo-second-order kinetic model were tested to find the best fitted model for the experimental data. The kinetic model equation:

\begin{align*}
\text{pseudo-first-order} & : \log (q_e - q_t) = \log q_e - (k_1t)/2.303 \\
\text{pseudo-second-order} & : \frac{t}{q_t} = \frac{1}{(k_2q_e^2)} + \frac{t}{q_e}
\end{align*}
3. Results and Discussion

3.1. Pyrolysis
According to Figure 3.1, it shows that RHB350 has the highest percentage yield but the biochar produced was brownish in colour which indicate incomplete of biochar pyrolysis. This is because lower pyrolytic temperature pyrolyzed lower amount of biomass composition and the biochar was not fully pyrolyzed. RHB400 and RHB450 were partially pyrolyzed because some of the biochar still in brownish in colour. Both RHB500 and RHB550 were fully pyrolyzed in high temperature and showed black in colour.

![Figure 3.1. Percentage yield of biochar produced](image)

3.2 Characterization

3.2.1 Moisture and ash content analysis. Based on Figure 3.2, it shows that the weight loss of drying process in moisture content analysis is attributed to the evaporation of water [6]. The moisture content of biochar decreased as the increased of pyrolytic temperature increased. The moisture decreased from 6.44% at 350°C to 3.73% at 550°C. RHB350 was the highest moisture content because of incomplete pyrolysis. The weight loss of burning process in ash content analysis is attributed to the production of ash [6]. The ash content of biochar increased as the increased of pyrolytic temperature increased. Form the pyrolysis process, RHB350, RHB400 and RHB450 were incomplete pyrolyzed hence the ash content was lower. Comparing with RHB500 and RHB550, both has higher ash content which they were fully pyrolyzed.
3.2.2 **FTIR (Fourier-transform infrared spectroscopy)**. According to Figure 3.4, it shows that the adsorption peaks located at the range of 3500-3300 cm\(^{-1}\) corresponded to the stretching of OH groups preferably from aliphatic alcohols and phenols and also assigned to N-H stretching [7]. The intensity of the peak at 3407.55 cm\(^{-1}\) decreased rapidly from raw sludge to biochar samples. The peak at 1599.69 cm\(^{-1}\) indicated high aromaticity and corresponded to presence of alkyl and alkene groups (C-H, C-C and C=C) from the stretch of aromatic rings [8]. The functional groups were observed such as C-C bonds and C=C double bonds in biochar. Lastly, the peaks allocated between 1099 and 798.79 cm\(^{-1}\) could be attributed to the phosphate groups. It also may be due to the stretching of silicon containing groups (Si-O-Si) given that rice usually has large amounts of silicon [7].
3.2.3 pH zero point charge ($pH_{zpc}$). The point of zero charge of each biochar was obtained from a plot of initial solution pH against equilibrium solution pH [5]. The purpose of pH zero charge is to determine the pH at which the biochar has zero charges. The zero-point charge ($pH_{zpc}$) of each biochar sample was determined.
3.3 Adsorption process

3.3.1 Contact time. Based on Figure 3.6, it indicates that the adsorption capacity increased rapidly in the initial of 30 minutes but then reduce afterward. At 180 minutes, the adsorption reached the equilibrium as the values of adsorption capacity of ammonium from 180 to 300 minutes were approximately constant. Ammonium adsorption reached equilibrium stage after 180 minutes as further increased in adsorption contact time does not enhance the ammonium adsorption. Hence, 180 minutes was chosen as the optimum adsorption contact time.

![Figure 3.6](image)

**Figure 3.6** Graph of adsorption capacity of ammonium $q_t$ (mg/g) versus contact time (min)

3.3.2 Adsorbent dosage. Figure 3.7 shows that at lower adsorbent dosage, the number of active sites was higher. The increased of adsorbent dosage, the decreased the adsorption capacity of ammonium. The decreased in the dosage were resulting in the increased of ammonium uptake [10]. In addition, the decrease in adsorption capacity may be also due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles. It was observed that when the biochar concentration ranged between 0.05g and 0.1g, there had higher adsorption capacity.

![Figure 3.7](image)

**Figure 3.7** Graph of Adsorption Capacity of Ammonium $q_t$ (mg/g) versus Adsorbent Dosage (g)

3.3.3 Initial concentration of ammonium. The adsorption capacity of ammonium was increased with the increased of initial concentration as shown in Figure 3.8. This is because the higher the initial ammonium concentration, it provided a greater driving force [10]. This is due to the increase in collision forces
between NH$_4^+$ ions in solution which break the resistance forces on the surface of both adsorbents. As the result, 1.2 ppm of ammonium concentration was chosen to be the constant initial due to its highest adsorption capacity. The increased the initial concentration of ammonium, the increased of the adsorption capacity of ammonium.

![Graph of Adsorption Capacity of Ammonium $q_t$ (mg/g) versus Initial Concentration of Ammonium (ppm)](image)

**Figure 3.8** Graph of Adsorption Capacity of Ammonium $q_t$ (mg/g) versus Initial Concentration of Ammonium (ppm)

### 3.4 Desorption process

Desorption was studied in batch experiment using 1% of NaCl solution. The use of NaCl is based on the selectivity order of ammonium among cations. The adsorption efficiency slightly decreased with the increased of cycle times as shown in Figure 3.9. The desorption efficiencies were slightly increased with the increased of cycle times. From the result, it can be concluded that rice husk biochar is a profitable biochar as it can continuous for 5 cycles.

![Desorption process](image)

**Figure 3.9** Desorption process

### 3.5 Kinetic Study

The adsorption kinetic was performed by varied adsorption contact time which was 1, 5, 10, 30, 60, 120, 180, 240, and 300 minutes in order to proceed kinetic fitting and determine adsorption rate. Both graphs of pseudo-first-order and pseudo-second-order show different behaviors. The value of R$^2$ of pseudo-
second-order modal was 0.9995 which nearer to 1 compared to pseudo-first-order, 0.9779. Thus, pseudo-second-order model was more preferable for adsorption kinetic which the value of $R^2$ is nearer to 1 that indicate a good mathematical fit.

![Graph of pseudo-first-order](image1.png)

**Figure 3.10** Graph of pseudo-first-order.

![Graph of pseudo second order](image2.png)

**Figure 3.11** Graph of pseudo second order.

4. **Conclusion**

RHB500 was selected as the best biochar for the ammonium adsorption process due to the characterization of moisture analysis, ash analysis, pH zero charge, FTIR Spectroscopy and SEM. Adsorption capacity of ammonium was increased rapidly at the initial contact time of adsorption process and then gradually slowed until reached the equilibrium contact time. At 180 minutes, the adsorption reached the equilibrium which the adsorption capacity was remained constant after the equilibrium time.

The adsorption capacity of ammonium was decreased when the adsorbent dosage increased. At 0.1g of adsorbent dosage, the adsorption capacity was the highest due to it availability of adsorption site for ammonium removal. Lastly, the adsorption capacity of ammonium increased when the ammonium initial concentration increased. The increment of adsorption capacity of ammonium was due to the saturated concentration of ammonium when high initial concentration of ammonium was tested. For adsorption-desorption, 1% NaCl solution was used to desorb the ammonium. The RHB was profitable as it reached up to 5 cycles of adsorption-desorption test.
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