Ammonia nitrogen removal from aqueous solution by local agricultural wastes

I Azreen, Y Lija, and A Y Zahrim
Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400, Kota Kinabalu, Sabah, Malaysia
E-mail: azreen@ums.edu.my

Abstract. Excess ammonia nitrogen in the waterways causes serious distortion to environment such as eutrophication and toxicity to aquatic organisms. Ammonia nitrogen removal from synthetic solution was investigated by using 40 local agricultural wastes as potential low cost adsorbent. Some of the adsorbent were able to remove ammonia nitrogen with adsorption capacity ranging from 0.58 mg/g to 3.58 mg/g. The highest adsorption capacity was recorded by Langsat peels with 3.58 mg/g followed by Jackfruit seeds and Moringa peels with 3.37 mg/g and 2.64 mg/g respectively. This experimental results show that the agricultural wastes can be utilized as biosorbent for ammonia nitrogen removal. The effect of initial ammonia nitrogen concentration, pH and stirring rate on the adsorption process were studied in batch experiment. The adsorption capacity reached maximum value at pH 7 with initial concentration of 500 mg/L and the removal rate decreased as stirring rate was applied.

1. Introduction
Nitrogen is a vital nutrient for living organism but excess of it in waterways will result depletion of dissolved oxygen, eutrophication and toxicity to fish and other aquatic organisms [1]. Ammonia nitrogen (NH₃-N) is one of the most common and toxic species of nitrogen and contamination of ammonia nitrogen in waterways have become one of the biggest environmental challenges recently. This pollutant usually found in municipal sewage, domestic and industrial wastewater or decomposed from organic N compounds in those wastewater and wastes [2]. The ammonia nitrogen discharged to the environment is strictly regulated and the maximum limit for ammonia nitrogen discharged onto waterways is 5 mg/L according to the Department of Environment Malaysia [3].

Various treatment methods of ammonia nitrogen have been developed such as chemical precipitation, ion exchange, adsorption, air stripping, biological nitrification and de-nitrification. Adsorption is one of the most attractive methods which are easy, effective and economical feasible [4] compared to others as the conventional methods are high in cost and complicated operation [5].

The utilization of agricultural biomass as biosorbent has been studied extensively as it offers economic and environmental friendly. Agricultural waste is convenient for experimental purpose as they are cheap, abundance and unlimited [6]. Besides, low cost adsorbent also can reduce the production of solid waste in Malaysia and they can be used as composting material and fertilizer after the adsorption process compared to conventional adsorbent such as activated carbon and zeolites [7].

The effectiveness of biosorbent in removing variety of pollutants such as dyes [8, 9], heavy metals [10], and phenolic compound [11] has been reported by many researchers. However, the availability
on the information of ammonia nitrogen removal by biosorbent is still limited. Hence, this study was intended to study the ability of 40 potential local biosorbent for adsorption of ammonia nitrogen. Biosorbent with highest adsorption capacity then was analyzed further for the effect of initial concentration of ammonia nitrogen solution, pH and stirring rate on the adsorption process.

2. Materials and methods

2.1. Preparation of adsorbents
A total of 40 local biomasses were collected from area of Kota Kinabalu, Sabah. The samples were washed thoroughly with tap water to remove dust and impurities. Then, the samples were cut into small pieces and washed again with distilled water. Next, the samples were allowed to dry in an oven at 40°C for 48 hours. The dried materials were crushed and grounded to desired size (1-2 mm).

2.2. Preparation of stock solution
Synthetic ammonium (NH$_4^+$) solutions were used throughout the adsorption experiments. Ammonium chloride salt (NH$_4$Cl) with calculated weight was dissolved in 1L of distilled water for desired concentration. The initial pH value of solution was adjusted to 7.0 using dilute solution of 0.1 M of sodium hydroxide (NaOH).

2.3. Screening experiment
The screening processes of each 40 samples were conducted by mixing 20 g of adsorbent in 500 mg/L of synthetic solution for 40 minutes of contact time. The final concentration of NH$_3$-N solution was determined by using UV-Vis spectrophotometer and adsorption capacity can be calculated.

2.4. Characterization of adsorbent
The characterization of adsorbent was assessed by zeta potential test. The zeta potentials of the adsorbent were determined at different pH value ranged from pH 3 to pH 10. This experiment was conducted in triplicate by using Malvern Instruments Zetasizer Nano-ZS and the results averaged.

2.5. Batch adsorption experiment
Batch adsorption experiments consisted of analysing the respective effect of initial stock solution concentration, pH and stirring rate on the adsorption of NH$_3$-N from aqueous solution. The sample with highest adsorption capacity obtained from screening experiments was selected for equilibrium characteristics study of NH$_3$-N adsorption.

The effect of initial ammonia nitrogen concentration was performed by using concentration range from 5 to 1000mg/L. Effect of initial pH was assessed by varying pH range from pH 3 to pH 11. Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) solutions were used for pH adjustment and the volume added for pH adjustment must be not exceeding 1% of the solution volume. The effect of stirring rate on ammonia nitrogen adsorption was assessed by using stirring rate range from 5 to 200 rpm. These experiments were conducted at room temperature and mass of samples and contact time were fixed to 20 g and 40 minutes respectively. Each experiment was made at least in two runs and result is averaged.

The adsorption capacity, q (mg/g) and removal rate (%) of NH$_3$-N were calculated for screening and batch adsorption experiment. Both equations are shown below respectively:

\[ q = \frac{(C_0 - C_f) V}{M} \]  \hspace{1cm} (1)

\[ \text{Removal rate (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \]  \hspace{1cm} (2)
where \( q \) (mg/g) is the adsorption capacity, \( C_0 \) (mg/L) and \( C_t \) (mg/L) are respectively the initial and at
time \( t \) ammonia nitrogen concentrations, \( V \) is the volume of aqueous solution (L) and \( M \) is the mass of
sample used as adsorbent (g).

3. Results and discussion

3.1. Screening experiment

The results shows that 18 out of 40 samples were able to adsorb ammonia nitrogen from the aqueous
solution and the rest of the samples show negative values. The negative values may be due to ammonia
nitrogen adsorbed from solution was less than the ammonia nitrogen released in these samples [12].

Table 1 shows the adsorption performances of 40 samples. Langsat peels (LP) show the highest
adsorption capacity with 3.58 mg/g and followed by Jackfruit seeds (JS) and Moringa Oleifera peels
(MOP) with adsorption capacity of 3.37 mg/g and 2.64 mg/g respectively.

Screening experiment conducted in this study suggested that some of the local agricultural wastes
have potential to be used as adsorbent for removal of NH\(_4^+\) ions. Agricultural biomass is an organic
compound comprised of cellulose, hemicelluloses, lignin, lipids, proteins, hydrocarbons, starch and the
samples may contain polar functional groups, such as alcohols, aldehydes, ketones, carboxyl, phenol
and ether groups. These constituents have the ability to bind pollutants to some extent [13] thus
making the adsorption of ammonia nitrogen is possible on the surface of agricultural biomass. Despite
having the highest adsorption capacity, JS was selected over LP for further adsorption equilibrium
characteristics study due to its availability throughout the years compared to LP and the adsorption
capacity of JS is not much difference with LP. Previous studies proved that JS can be utilized as
adsorbent for pollutant removal such as dye [14] and heavy metal [15].

Jackfruit seed is high in starch content with approximately 93 to 95% [16] and the starch consists of
two macromolecules: amylose (20-30%) and amylopectin (70-80%), which are associated with each
other by hydrogen bonds [17]. Amylose is a linear polymer consisting mainly \( \alpha \)-1, 4 linked D-glucose
units and Amylopectin consists of branched polymer comprised of \( \alpha \)-1, 4 linked glucose units with \( \alpha \)-
1, 6 branching links [18]. The structure and physicochemical properties of starch are depending on
these macromolecules content and it can affect the sorption performance of starch [19]. The ability of
starch to adsorb NH\(_4^+\) ions may arises from the electrostatic force of attraction between the anion from
the sample surface and the positively charged NH\(_4^+\) ions [20].

The characterization of adsorbents used in this experiment was studied by zeta potential test. The
magnitude and sign of surface charge of a solid immersed in a water solution are related to zeta
potential that occurs at the slipping plane of the solid. Thus, this test is used for measuring the
potential of solid at the shear plane to characterize its electro-kinetic behaviour [21]. Zeta potentials of
40 agricultural biomasses at pH 7 were determined and presented in Table 1. The zeta potential
properties of JS over pH range of 3-10 were further analysed and results depicted in Figure 1.

The adsorbent exhibits negative value of zeta potential over the entire range of pH value and
become more negative as the pH increases. This condition is favourable for ammonium adsorption due
to the attraction between the negatively charged adsorbent and the positively charged adsorbate species
[13]. This result is in accordance with previous studies that report on the dependency of zeta potential
over pH value [22-24].
Figure 1. Zeta potential against pH value for Jackfruit seeds

Table 1. Adsorption capacity and removal rate of 40 local biosorbent.

| Waste                  | Scientific Name       | Removal rate (%) | Adsorption capacity (mg/g) | Zeta potential (mV) | Season (month)                      |
|------------------------|-----------------------|------------------|----------------------------|---------------------|------------------------------------|
| Banana peel            | Musa Acuminata        | 8.22             | 1.51                       | -27.4               | Jan-Dec                            |
| Banana comb            | Musa Acuminata        | 7.03             | 0.88                       | -51.37              | Jan-Dec                            |
| Papaya peel            | Carica Papaya         | -4.96            | -0.81                      | -32.4               | Jan-Dec                            |
| Papaya seed            | Carica Papaya         | -17.3            | -3.03                      | -31.6               | Jan-Dec                            |
| Pomelo peel            | Citrus Maxima         | 13.95            | 1.74                       | -29.0               | Aug-Oct / Jan-Mar                   |
| Pineapple peel         | Ananas Comosus        | -39.07           | -4.88                      | -12.4               | Jan-Dec                            |
| Pineapple stem         | Ananas Comosus        | 2.93             | 1.07                       | -14.0               | Jan-Dec                            |
| Langsat (Lanzones) peel| Lansium Domesticum    | 28.67            | 3.59                       | -36.3               | Jun-July / Nov - Feb               |
| Langsat (Lanzones) seed| Lansium Domesticum    | 5.36             | 0.79                       | -48.3               | Jun-July / Nov - Feb               |
| Soursop peel           | Annona Muricata       | -1.96            | -0.25                      | -22.4               | March - April / June - July        |
| Coconut coir           | Cocos Nucifera        | 12.73            | 1.59                       | -37.9               | Jan-Dec                            |
| Sugarcane bagasse      | Saccharum Officinarum | 3.67             | 1.59                       | -20.3               | Jan-May                            |
| Corn (silk)            | Zea Mays              | -3.74            | -4.68                      | -37.87              | Jan-Dec                            |
| Corn (shank)           | Zea Mays              | -7.56            | -0.95                      | -22.75              | Jan- Dec                           |
| Corn comb              | Zea Mays              | -10.45           | -1.56                      | -23.7               | Jan- Dec                           |
| Corn husk leaf         | Zea Mays              | 5.55             | 0.69                       | -20.15              | Jan- Dec                           |
| Passion fruit          | Passiflora Edulis     | 6.34             | 0.79                       | -35.1               | Nov-April                          |
| Cassava peel           | Manihot Esculenta     | 5.81             | 0.73                       | -40.11              | Jan-Dec                            |
| Banana false stem (Pseudostem) | Musa Acuminata      | -3.14            | -0.39                      | -32.6               | Jan-Dec                            |
| Sapodilla peel         | Manilkara Zapota      | -73.16           | -9.32                      | -11.9               | Jan-Dec                            |
| Limau madu (Citrus) peel| Citrus Suhuensis      | 15.59            | 1.95                       | -38.05              | March-April / Oct-Nov              |
| Jackfruit peel         | Artocarpus Heterophyllus | 16.26          | 2.03                       | -18.03              | Jan - Dec                          |
| Jackfruit seed         | Artocarpus Heterophyllus | 26.96          | 3.3702                     | -24.8               | Jan - Dec                          |
3.2. Effect of initial stock solution concentration

The effect of initial NH$_3$-N concentration on adsorption process by JS was studied by varying the concentration in a range of 5 to 1000mg/L. The concentration range used in this study is based on typical range of NH$_3$-N concentration from landfill leachate [25] and industrial wastewater [26]. The experiments were carried out at room temperature with adsorbent dosage of 20 g and 40 minutes of contact time. The variation in the sorption of NH$_3$-N as a function of concentration is depicted in Figure 2.

Increasing the initial stock solution concentration lead to an increase in the ammonium (NH$_4^+$) ions uptake by JS, however the adsorption capacity decreased at 1000 mg/L of solution. The increase in NH$_4^+$ ions uptake may be due to the increasing driving force of the concentration gradient as the initial concentration increased [7]. As the initial concentration increased to 1000mg/L, the adsorption capacity decreased to 1.34 mg/g. This behaviour can be explained due to the insufficient surface sites of an adsorbent. Since the concentration of solution increased, more sites on the surface of JS were taken up [27].

| Plant Part               | Species                  | At (%) | Analytical Value (%) | Pesticides (%) |
|-------------------------|--------------------------|--------|----------------------|----------------|
| Areca palm              | Areca Catechu            | -4.32  | -0.54                | -31.9          | Jan- Dec     |
| Coconut mesocarp        | Cocos Nucifera           | -72.0  | -10.08               | -29.7          | Jan -Dec     |
| Honey Dew peel          | Cucumis melo var. inodorus | -5.79  | -0.72                | -27.2          | Jan- Dec     |
| Purple Yam peel         | Dioscorea Alata          | -43.05 | -5.38                | -47.1          | Jan-Dec      |
| Mango seed              | Mangifera Indica         | -78.65 | -9.78                | -42.07         | Jan-Dec      |
| Mango peel              | Mangifera Indica         | -3.74  | -0.47                | -26.23         | Jan-Dec      |
| Sweet potato peel       | Ipomoea Batatas          | 6.97   | 0.87                 | -19.53         | Jan-Dec      |
| Cat’s Eye (Mata Kucing) | Euphoria Malaiense       | -52.93 | -6.62                | -27.1          | Jan-Feb      |
| Mata Kucing (Cat’s Eye) | Euphoria Malaiense       | -2.37  | -0.36                | -28.4          | Jan-Feb      |
| Moringa peel (young)    | Moringa Oleifera         | -76.33 | -9.54                | -42.33         | Jan-Dec      |
| Moringa seed (young)    | Moringa Oleifera         | -6.99  | -0.87                | -28.37         | Jan-Dec      |
| Moringa peel (mature)   | Moringa Oleifera         | 21.09  | 2.64                 | -44.07         | Jan-Dec      |
| Moringa seed (mature)   | Moringa Oleifera         | -7.35  | -0.92                | -9.47          | Jan-Dec      |
| Breadnut stem           | Artocarpus Camansi       | -4.32  | -0.64                | -25.8          | Jan-Dec      |
| Breadnut peel           | Artocarpus Camansi       | 10.97  | 1.37                 | -35.2          | Jan-Dec      |
| Bambangan peel          | Mangifera Pajang         | 4.67   | 0.58                 | -21.8          | May-Nov      |
| Bitter bean (Petai)     | Parkia Speciosa          | -1.43  | -0.18                | -50.5          | Aug-Sept     |
3.3. Effect of initial pH

The initial pH solution is one of the most critical controlling parameters in adsorption processes. The effect of initial pH on the adsorption process was observed by taking the common pH values of wastewater where the value lies in range of 3 to 11. The adsorption capacity of ammonia nitrogen removal at different pH is shown in Figure 3 for the initial solution concentration of 500 mg/L. The adsorption capacity of JS on the NH$_3$-N removal process shows negative value at pH 3, increased to 0.69 mg/g at pH 5 and reached maximum adsorption capacity (3.37 mg/g) at pH 7. The adsorption values decreased to 0.44 mg/g as the pH value increased to pH 9 and reached negative value at pH 11.

The negative values of adsorption capacity obtained are due to amount of ammonium released more than amount adsorbed. Low adsorption capacity obtained at lower pH is mainly attributed to the facts that more hydrogen (H$^+$) ions is present in the aqueous solution thus making H$^+$ ions compete effectively with NH$_4^+$ cations [28]. Increasing the pH value to pH 7 seems favorable for the adsorption process as the adsorption capacity increased along with it. This might be due to the fact that the fibers chains become negatively charged at higher pH and thus enhance the replacement of exchangeable cations present at the exchangeable sites in the aqueous solution through attraction forces [5]. At higher pH, NH$_4^+$ is neutralized by hydroxyl (OH$^-$) ion and OH$^-$ compete for NH$_4^+$ with the active sites on the surface of the adsorbent thus lower the adsorption capacity [29].

3.4. Effect of stirring rate

Figure 4 shows the adsorption capacity of jackfruit seed at different stirring rate range from 0 to 200 rpm with contact time of 40 minutes. The effect of stirring rate at static conditions is important to be
investigated since it will give a better understanding about nutrients adsorption capacity from wastewater onto lignocellulosic fibers [30, 31]. The ability of adsorbent to remove pollutant in moving or fast-flowing water can be evaluated as the stirring speed increases. Maximum adsorption occurred when no stirring rate was applied to the solution where the adsorption capacity reached 3.37 mg/g. The adsorption capacity of JS slowly decreased as the stirring rate increased and reached negative value at highest stirring rate applied. This reduction is related to the fact that rotation caused the ammonium ions which bind to the adsorbent to be released again and ammonia nitrogen molecules does not have enough time to come into contact with the sorbent at higher speeds [32].

![Figure 4](image_url)

**Figure 4.** Effect of stirring rate on adsorption capacity of Jackfruit seeds.

4. Conclusions

The ability of 40 agricultural wastes as potential low cost adsorbent for ammonia nitrogen removal was tested in this study. The experimental findings suggested that 18 out of 40 samples were able to remove ammonia nitrogen with highest adsorption capacity of 3.58 mg/g. Jackfruit seed was chosen for further equilibrium characteristic analysis due to its availability and high adsorption capacity. Maximum adsorption occurred at pH 7 with initial ammonia nitrogen concentration of 500 mg/L.

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