Adsorption of Ammonium Ions Using Activated Carbon Derived from *Artocarpus odoratissimus* Skin

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Abstract. Wastewater consists of various contaminants including ammonium ions, which are toxic to aquatic life if the concentration exceeds the standard limit. The need for finding an effective treatment to remove the pollutant is crucial, as it is difficult to remove it due to its resistance and tenacity to the environment. In this study, *Artocarpus odoratissimus* or commonly known as “*Tarap*” skin (TS) was used as a precursor for the preparation of activated carbon (AC) by two-step KOH activation. The TS was pyrolysed first at 350 °C prior to KOH activation at 1:1 of impregnation ratio and 800 °C of activation temperature under nitrogen gas flow in a tubular furnace. Percentage of yield, surface area, and porosity, morphology structure, surface functionalities and as well as the ability of TS based AC to adsorb ammonium ions were investigated and analysed. The properties of carbon showed that the carbon yield produced was 18.5% with a 1372.51 m²/g of surface area, 0.6756 cm³/g of pore volume and 2.1453 nm of average pore radius. The adsorption capacity of carbon at equilibrium was 1.858 mg/g. The isotherm model and kinetic study for adsorption of ammonium ions were studied using Langmuir and Freundlich, Pseudo-first order and Pseudo-second order, respectively. The equilibrium data obey the Langmuir isotherm model with the highest correlation ($R^2=0.9373$). As for the kinetic study, the adsorption process follows Pseudo-second order, which has $R^2$ value of 0.9964 and adsorption capacity, $q_e$ of 1.737 mg/g.

Introduction

Ammonium ions are a form of pollutants found in water bodies mainly in industrial wastewater, in which the accumulation of these ions in water course may result in the reduction of dissolved oxygen, biological eutrophication and toxicity into aquatic life (1–3). The principal source of the ammonium ions pollutions of surface and ground water resources are from agricultural activities, domestic and industrial effluent and runoff from waste disposal sites, construction sites and animal feed lots (4). The concentration of ammonium ions that exceed the allowable limit could harm the aquatic life, as fish and other forms of aquatic life exposures to toxic if the concentration of ammonium ions as low as 0.2 mg/L (2). Based on Environmental Quality (Industrial Effluent) Regulation, Department of Environment, Malaysia, the discharge limit for ammoniacal nitrogen into any inland waters within the catchment areas (Standard A) and any other inland waters or Malaysia waters (Standard B) are 10 mg/L and 20 mg/L, respectively (3). Thus, the removal of the ammonium ions is obligatory, however, its resistance and tenacity in the environment making it is important to find an efficient way to treat the pollutant.

There are several treatment methods such as physical, chemical, biological, or a combination of these methods, developed to remove the ammonium ions pollution in wastewater mainly including ion exchange, biosorption, adsorption reverse osmosis, microwave radiation, air stripping and chemical precipitation. One of the best treatment methods can be used to treat the wastewater is through...
adsorption technique as it is high affinity toward ammonium ions, high removal efficiency, easy to operate, economical feasible and environmental friendly, which these advantages make it broadly applied in large scale for commercial and water purification (6–14).

*Artocarpus odoratissimus* or commonly known as *tarap* skins (TS) are abundant agricultural waste from agricultural industries in Malaysia, especially in Sabah. The eatable part or flesh of these fruits is only about one-third while the rest are core, seeds and shell usually thrown away as waste. The high consumption of the fruits left dumping of the vast amount of peels. Nowadays, there is potential in utilizing waste generated from agricultural waste to convert it into a new sustainable product, such as activated carbon (AC), which is eco-environmentally (3,15–18). There are some examples AC prepared from these waste, including durian skin (19,20), *tarap* core (21), jackfruit skin and banana peel (20,21). Therefore, TS can be reused as a source of AC, which functions in removing undesirable odour, colour, taste and other organic and inorganic impurities from domestic and industrial wastewater (22,23). This is because the precursor consists of a high content of carbon, which is a suitable natural source for raw material of AC (24,25). The AC can be prepared via two methods, which are physical and chemical activation or combination of the two methods studied in the previous research. In physical activation, the carbonized char is done earlier or not, heating at high temperature in the inert atmosphere. In chemical activation, the carbon is first carbonized at a heating temperature lower than physical activation and followed by mixing the carbon with a chemical prior for the next heating process. Not only the type of precursor used, but the method of preparation process also affected the characteristics of activated carbon produced in terms of its percentage yield, porosity and morphology structure (26).

In wastewater treatment, there are standard discharge limits of chemical concentration into water bodies. The characteristics of the pollutants itself are varied, such as ammonium ions, a type of contaminant existed in wastewater, that is hard to eliminate due to its resistance and tenacity to water. ACs are becoming promising adsorbent used in wastewater purification these days. The great performance of the AC in removing pollutant such as ammonium ions in wastewater compared to other adsorbent making it feasible. The commercial AC derived from synthetic material such as zeolites, polymers, silica gel, and alumina are expensive due to high cost of production, which make it less feasible, and meanwhile, it has great performance in removing pollutant. However, the cost limitation has contributed to the need for finding alternative material for low cost adsorbent. In addition, the accumulation of agricultural waste such as TS on land without any further treatment contributes to land pollution. Furthermore, the effectiveness of an AC is measured on its adsorptive abilities, and is influenced by its characteristics especially its porosity properties. Therefore, the type of precursor and method of activation affect the properties of an activated carbon produced (26,27). Thus, the performance of a low-cost adsorbent derived from TS by adsorption of ammonium ions is studied. The application of AC derived from TS as an adsorbent used in wastewater treatment could significantly improve the wastewater industries as the treatment method utilized are low cost, high efficiency removal, easy to operate and sustainable. This study aims to prepare AC derived from TS using chemical activation, to characterize the physical and chemical properties of AC prepared and to investigate the performance of ammonium ions adsorption.

Methodology

1.1 Preparation of activated carbon

*Tarap* fruits were purchased from the local open market. The skin of *tarap* was separated from the rest of the fruits. The TS was cleaned and rinsed with distilled water. The TS was dried in an oven separately at 105°C until a constant mass was obtained. The dried TS samples were ground until it became powder. The ground samples for TS was weighted and put in a sealed container, and placed inside a desiccator. The pyrolysis process was carried out in single zone split tube furnace Thermolyne F79320-22 240V by placing the ground sample of TS inside a stainless steel crucible in the furnace. Nitrogen gas (N₂) was purged into the reactor to create an inert condition. The N₂ gas was injected into the system at a flow rate of 10 mL/min and the flow rate of N₂ gas was controlled using the flowmeter. The temperature was set up from room temperature to 350°C for 1 h (28). Then, the reactor was cooled...
down to room temperature. The char produced was stored in a sealed container and placed in the
desiccator for further treatment. In this study, TS based AC was prepared via two-step KOH
activation. In the first step, the TS was pyrolysed first. For pyrolysis, the dried TS was undergone
lowest pyrolysis temperature at 350°C. This was to ensure the hemicellulose in TS decomposed (29).
In the second step, the char from TS was chemically treated with KOH, which act as a chemical agent
and activated at 800°C. The gasification reaction results in enlargement of porosity of the carbon by
KOH activation. From the reaction of KOH and carbon occurs according to the reaction as in equation
1, the KOH is reduced to metallic potassium during the carbonization (30).

\[
6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3
\]  

The presence of metallic potassium intercalate to the carbon matrix, which contributes in widening of
the spaces between carbon atomic layers and increasing the total pore volume (31). A similar trend of
finding was reported in the production of cassava peel activated carbon via KOH activation (32).

1.2 Impregnation with the chemical agent
The carbonized char was impregnated with potassium hydroxide (KOH) act as chemical agent at
different ratios. The char was treated with KOH by mixing it with a concentrated solution of KOH in a
beaker (33) with an impregnation ratio of 1:1 (KOH: char). The TS sample was evaporated at 80°C for
24 h in the oven. The dried mixture of KOH-impregnated char of TS was obtained.

1.3 Activation process
The activation process was carried out by placing the KOH impregnated char of TS sample inside a
stainless steel crucible in the horizontal tube furnace. The temperature was set up from room
temperature to 850°C of activation temperature for 1 h (28). Then, the reactor was cooled down to
room temperature by letting the N\textsubscript{2} flowed in the tube continuously. After the reactor cooled down, the
channel of N\textsubscript{2} flow was closed. The sample was taken out from the tube furnace. The schematic
diagram of equipment set up for activation process is shown in Figure 1.

![Figure 1. Schematic setup for AC activation process](image-url)

1.4 Washing process
The activated sample of TS produced was washed with 1M hydrochloric acid (HCl) and followed by
further washed with warm distilled water several times until the pH of the washing solution reached
6.5-7. The washed sample of TS was filtered using filter paper and dried in the oven at 105°C for 24 h
or until obtained a constant mass. The AC from TS (TSAC) produced was weighed and stored in a
sealed container and kept in the desiccator for further characterization and adsorption experiments.
The yield of TSAC was calculated using equation 2 (34):
Yield (%) = \( \frac{w_a}{w_g} \times 100 \)  \hspace{1cm} (2)

where \( w_a \) and \( w_g \) are the dry weight of TSAC (g) and the dry weight of precursor (g) respectively.

1.5 Characterization of AC

There are several characterization analysis experiments carried out in this study such as percentage yield, surface area and porosity, morphology structure and surface functional group of TSAC.

1.5.1 Surface area and porosity

The surface area and porosity of the TSAC were analysed by nitrogen adsorption using the Brunauer-Emmett-Teller (BET) technique. The BET surface area and pore size distribution were determined from nitrogen isotherm at 77.3 K using Quanta chrome autosorb automated gas sorption instrument. Prior to analysis, the adsorbents are out gassed for 12 h under vacuum at 110°C. The specific surface area was determined according to the BET method at the relative pressure of 0.99 (7-10).

1.5.2 Morphology structure

The analysis of morphology structure and pore development of the TSAC was performed using scanning electron microscopy (SEM), Carl Zeiss MA10. Before SEM analysis, the samples were dried at 110°C for 24 h. The granular form of TSAC sample was used to search for porous structure of sample (7-10).

1.5.3 Surface Chemistry

The surface functional groups of the precursor and TSAC were analysed by Fourier Transform Infrared (FTIR) spectroscopy. First, the prepared TSAC samples were grinded and dried at 110°C for 24 h. Then, required amount of grinded sample was put into the FTIR spectrophotometer to obtain IR spectrum. The IR spectrum was obtained at a resolution of 1 cm⁻¹ over the range 4000-800 cm⁻¹ from the spectrometer (7-10).

1.6 Adsorption experiment

The performance of TSAC was investigated through the removal of ammonia ions through the adsorption process. The ammonia nitrogen adsorbate was obtained from the preparation of ammonia chloride (NH₄Cl). The adsorption experiments were carried out by introducing the ACs that acted as adsorbent, into NH₄Cl adsorbate. There are several parameters studied for removal of ammonium ions such as the effect of initial adsorbate concentration, adsorbent dosage and temperature of the solution. NH₄Cl was prepared to get ammonium ions adsorbate with an initial concentration of 50 mg/L. The weight ratio (mg/g) of 50 mg/L was calculated as follows.

\[ \frac{50 \text{ mg}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ g of distilled water}} = 0.05 \text{ mg/g} \]  \hspace{1cm} (4)

Thus, 50 mg of NH₄Cl was diluted in 1000 g of distilled water to get 50 mg/g of NH₄Cl stock solution.

1.6.1 Batch Adsorption Studies

Batch adsorption experiment on the removal of ammonium ions was studied. There are several parameters were used to determine the adsorption capacity of AC. The effect of initial ammonium ions concentration, the solution temperature and dosage of adsorbent were the parameters used to investigate the ammonium ions removal. The final residual concentration of ammonium ions of the sample solution was withdrawn at intervals by using a UV-visible spectrophotometer at a wavelength of 425 nm (35). The concentration of ammonium ions adsorbed at equilibrium was calculated using equation 5.
\[ q_e = \frac{(C_0 - C_e)V}{w} \]  

(5)

where \( q_e \) (mg/g), \( C_0 \) (mg/L), \( C_e \) (mg/L), \( V \) (dm³) and \( w \) (g) are the concentration of ammonium ions adsorbed at equilibrium, liquid-phase concentrations of initial adsorbate and equilibrium, the volume of solution and mass of AC used, respectively.

2.6.2 Effect of contact time
The effect of initial ammonium ions concentration was studied by adding 2 g of TSAC into 200 mL of ammonium ions solution at 50 mg/L of initial concentration of NH₄Cl. The sample solution was stirred at 125 rpm using a digital stirring hot plate at 30°C of constant temperature until equilibrium was achieved. An amount of sample was taken at a period of time and filtered using filter paper. Then, the concentration of NH₄Cl was analysed by UV-visible spectrophotometer at 425 nm wavelength.

2.6.3 Effect of solution temperature
The effect of solution temperature was studied by adding 2g of a fixed amount of TSAC into 50 mL of 50 mg/L NH₄Cl solution and stirring the sample solution at 125 rpm using a digital stirring hot plate at various constant temperature (20, 30, 40 and 50°C) until equilibrium was achieved (36). Then, the concentration of NH₄Cl was analysed by UV-visible spectrophotometer at 425 nm wavelength.

2.6.4 Effect of adsorbent dosage
The effect of adsorbent dosage was studied by adding the various amount of TSAC (0.01, 0.10, 1.5 and 3.0 g) into 100 mL of 50 mg/L of ammonium ions solution. The sample solution was stirred at 125 rpm using a digital stirring hot plate at 30°C of constant temperature until equilibrium was achieved. Then, the concentration of NH₄Cl was analysed by UV-visible spectrophotometer at 425 nm wavelength.

Results and discussions

1.7 Characterization of AC
The yield of carbon was determined as the amount of carbon produced per amount of precursor. By using equation (3), the percentage yield of TSAC was calculated and found to be 18.5%. This is due to an activation temperature (37). At high activation temperature (more than 600°C of activation temperature), the yield of AC decreases as the weight loss rate is higher, which is mostly due to the initial large amount of volatiles that can be easily released with higher temperature, as well as the loss of moisture to a lesser extent. This report is to the similar finding of the previous study in which activation of corncob activated carbon was using KOH (38).

1.8 Surface area and porosity
Figure 2 and Figure 3 exhibit the nitrogen adsorption/desorption and pore size distribution of TSAC, respectively. The shape of the adsorption isotherm provides preliminary qualitative information on the adsorption mechanism and the porous structure of TSAC (39). It reveals the essential microporous nature of the TSAC. Initially, isotherm at very low pressure shows a sharp increase in typical adsorption taking place by primary filling of ultramicropores. At slightly higher \( P/P_0 \) and up to 0.1, adsorption is increased, which indicates a secondary filling of micropores. Adsorption volume also increases even though in a less degree, up to \( P/P_0 = 0.5 \), a range of relative pressure in which adsorption mechanism is by co-operative micropore filling of super micropores.

The TSAC shows a similar pattern of isotherm, which belongs to type IV isotherm. The hysteresis loop in the \( N_2 \) adsorption/desorption isotherm indicates the presence of mesopores (40). A similar trend of finding was observed in the earlier research, in which characterization of AC from bamboo sawdust by chemical activation with KOH(41). The surface area of TSAC was found to be 1372.51
m/g with a pore volume of 0.6756 cm³/g and the average pore radius was 2.1453 nm. From the data, the porosity of TSAC shows a good pore development and widening of a pore. The surface area of TSAC was affected by the burn-off of the AC and depends on the mass, removed during the activation of the carbon, which pores are formed to the material (42). Moreover, the development of pore for TSAC occurs during the KOH activation. This is probably due to the interior etching process of KOH activation, which promotes the formation of micropores (38). A similar result was obtained in the preparation and characterization of activated carbon from bamboo using KOH activation (43).

Figure 2. Nitrogen adsorption/desorption isotherm of TSAC

Figure 3. The pore size distribution of TSAC
1.9 Morphology structure
The technique used to observe the extrinsic pores on the carbon surface was SEM. In this study, the image at 1.50 KX magnification for the TAC sample was observed as shown in Figure 4.

Figure 4. SEM image of TSAC

Figure 4 reveals that the TSAC has a porous surface texture, which indicates that the prepared AC is highly porous. This approves that the TSAC has a large surface area. The existence of pore structure is due to the breakdown of lignocellulose at high temperature followed by evaporation of volatile compound and produced a well-developed pores (34). In addition, the increased reaction rate of C-KOH during the activation process at high temperature leads to carbon burn-off, thus good pores on the sample are developed. A similar finding was observed for the characterization of AC from *acacia nilotica* stalk by KOH activation (44).

1.10 Surface functionalities
The method used to characterize the surface chemistry of AC is using Fourier Transformed Infrared Spectroscopy (FTIR). Figure 5 shows the IR spectra of *tarap* skin precursor and activated carbon derived from TS. Figure 6 illustrates the IR spectra of AC before and after ammonium ion treatment. Figure 5 shows that the two new peaks are observed near 1650 and 1080 cm\(^{-1}\) for TSAC. This observation exhibits that the oxygen containing carbon reacts with KOH to form a carboxylic salt structure at peak 1650 cm\(^{-1}\). On the other hand, the peak at 1080 cm\(^{-1}\) is due to the C-O-C type structure. Hence, the two peaks could be seen. There is a similar finding reported, which preparation and characteristics of rice-straw based activated carbon via KOH activation (45). As can be observed in Figure 6, a poor profile of TSAC obtained after ammonium ions adsorption. However, there is a wide band at about 2700-3500 cm\(^{-1}\) after ammonium ions adsorption. This exhibits the O-H stretching and adsorbed water molecule. This shows a similar finding from the previous study, which adsorption of ammonium ion by coconut shell based AC (36).
1.11 Parameter studies on adsorption of NH\textsubscript{4}Cl

The adsorption of ammonium ions was affected by several factors including initial concentration, contact time, temperature and pH of solution and adsorbent dosage. In this study, the parameter used to investigate the adsorption of ammonium ions were contact time, adsorbent dosage and temperature of the solution.
1.11.1 Effect of contact time

The effect of contact time on the adsorption of ammonium ions was studied with 2 g of TSAC in 50 mg/L of NH₄Cl. Figure 7 (a, b, c) shows the concentration of ammonium ions against adsorption time, ammonium ions adsorption uptake against adsorption time and ammonium ions percentage removal against adsorption time at initial concentration of NH₄Cl of 50 mg/L, respectively.

![Figure 7](image)

Contact time is an important parameter that should be optimized in adsorption studies. This is due to ensure the adsorbent-adsorbate system reaches complete equilibrium upon contact with TSAC. Based on Figure 7(a), the final concentration of ammonium ions decreases rapidly in the first two hours period. Thereafter, it gradually slows down and reaches equilibrium at about 20 h. This shows that the ammonium ions adsorption uptake in the first two hours adsorption time is increasing rapidly with more than 30% removal. This indicates that the abundance of many vacant active sites on the surface of the adsorbent, thus allowing the ammonium ions molecules to be readily absorbed. Then, the adsorption uptake of ammonium ions slowly reaches equilibrium after 20 h of adsorption time. This means it reaches a point of saturation, in which there is the limited vacant site of TSAC for ammonium ions to adsorb onto. The available remaining surface sites are difficult to be occupied, due to the repulsion between the solute molecules and bulk phase of TSAC. Therefore, the optimum contact time required for the adsorption of ammonium ions onto TSAC was determined at 20 h. These findings are similar to previous studies, which adsorbed malachite green dye using durian seed AC(34), and Rhodamine B dye using tarap peel adsorbent (46).

1.11.2 Effect of solution temperature

The effect of adsorbent dosage on the adsorption of ammonium ions was studied with 2 g of TSAC in 50 mg/L of NH₄Cl at 20, 30, 40 and 50°C temperature of the solution. Figure 8 (a, b, c) shows the concentration of ammonium ions against the temperature of the solution and the percentage of ammonium ions removal with respect of solution temperature, respectively. Figure 8(a) shows that the concentration of ammonium ions increases when the solution temperature increase. The adsorption capacity against solution decreases as the temperature of solution increases as illustrated in Figure 8(b). Figure B(c) shows that the highest ammonium ions removal percentage is about 50% and 38% at 20°C and 30°C of solution temperature, respectively. This indicates that the ammonium ion exchange capacity was more favourable at a lower temperature (36). The adsorption rate is slow in the process of chemical adsorption, and the increase in temperature may favour the improvement of the adsorption rate. Nevertheless, too high temperature is unfavorable to exothermic reaction once it reaches the
equilibrium. Thus, there is a tendency for the ammonium ion to desorb from the solid adsorbent to the bulk solution phase with an increase in the temperature. A similar finding was reported for the adsorption ammonium ions using coconut shell AC (36).

![Figure 8](image_url)

**Figure 8.** (a) Concentration of ammonium ions against the temperature of solution (b) Ammonium ions adsorption uptake against the temperature of the solution (c) Ammonium ions removal percentage against the temperature of the solution (50 mg/L; 2 g; 50 mL; pH 7)

1.11.3 Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of NH₄Cl was studied with 0.01, 0.5, 1.5 and 3.0 g of TSAC in 50 mg/L of NH₄Cl. Figure 9 (a, b, c) shows the concentration of ammonium ions against adsorbent dosage, ammonium ions adsorption uptake against adsorbent dosage at an initial concentration of NH₄Cl of 50 mg/L and the percentage of ammonium ions removal with respect of adsorbent dosage, respectively.

![Figure 9](image_url)

**Figure 9.** (a) Concentration of ammonium ions against the adsorbent dosage (b) Ammonium ions adsorption uptake against the adsorbent dosage (c) Ammonium ions percentage removal against the adsorbent dosage (50 mg/L; 30°C; 100 mL; pH 7)
Figure 9 (a,b) show that the concentration of ammonium ions decreases as the adsorbent dosage increases, in which there is an increase in ammonium ions adsorption uptake as the adsorbent dosage is increasing. This is probably due to the higher surface area and more adsorption sites arising from the increase in adsorbent dosage (47). As shown in Figure 9(c), 3g of adsorbent dosage gave the highest ammonium ions percentage removal, which about 40%. Similar finding observed for removal of chlorinated phenols using coconut shell AC (47) and papaya seed AC (12).

1.11.4 Adsorption isotherm study

The relationship between the number of ammonium ions adsorbed at constant temperature and concentration in the equilibrium solution were tested using the two most commonly used linear isotherms, which are Langmuir and Freundlich isotherms. The comparison between the correlation coefficient is used to determine the applicability of the system. Figure 10 (a) illustrates the graph of $\frac{q_e}{C_e}$ against $C_e$ for Langmuir isotherm and the value of $q_{max}$, $K_L$ and $R_L$ were calculated from the graph. Figure 10 (b) shows the plot graph of log $q_e$ against log $C_e$ for Freundlich isotherm and the value of $n$ and $K_F$ were obtained from the graph. The value of rate constant $K_L$, $K_F$, $\frac{1}{n}$, $q_{max}$ and regression coefficient ($R^2$) for the Langmuir and the Freundlich are summarized in Table 1. From Table 1, the value of Langmuir $R^2$ for TSAC (0.9373) is higher than the Freundlich $R^2$ value (0.7767). It shows the Langmuir model fits the data better suggesting the ammonium ions adsorption much occurs by chemisorption within the monolayer (48).

![Figure 10. (a) Langmuir isotherm plot (b) Freundlich isotherm plot](image)

**Table 1. Isotherm model of TSAC**

| Model isotherm | Parameters                  | Adsorbent |
|---------------|----------------------------|-----------|
| Langmuir      | $q_{max}$ (mg/g)            | 0.303     |
|               | $K_L$ (L/g)                 | 0.06      |
|               | $R_L$                       | 0.20      |
|               | $R^2$                       | 0.9373    |
| Freundlich    | $\frac{1}{n}$              | 1.07      |
|               | $K_F$ (L/mg)                | 21.54     |
|               | $R^2$                       | 0.7767    |
1.11.5 Adsorption kinetic study

The kinetic study used for adsorption of number of ammonium ions by TSAC were pseudo-first order and kinetic pseudo-second order. These kinetic studies were used to determine the rate and kinetics of ammonium ions removal onto activated carbon prepared. The suitable model for the adsorption of ammonium ions was determined according to the unity of regression coefficient ($R^2$). Figure 11 (a) shows the plot graph of $\log (q_e - q_t)$ against $t$ for Pseudo-first order and the rate constant of $k_1$ (min$^{-1}$) and $q_e$ are calculated. Figure 11 (b) illustrates the plot graph of $\frac{t}{q_t}$ against $t$ for Pseudo-second order and rate constant of $k_2$ (g/mg.min) and $q_e$ are calculated. Table 2 summarizes the $q_{e,cal}$, $k_1$, $k_2$, and $R^2$. The calculated $q_e$ are compared to the experimental value. The value of $q_{e,cal}$ for Pseudo-second order (1.7367 mg/g) closes to the experimental value (1.858 mg/g) compare to Pseudo-first order (1.008 mg/g). The $R^2$ of Pseudo-second order (0.9964) is higher than Pseudo-first order (0.7957). Therefore, the results suggest that the adsorption of ammonium ion by TSAC follows the Pseudo-second order. It can be said that more than one step may involve in the adsorption process, which diffusion of ammonium ions from the bulk solution to the external surface of adsorbent or boundary layer diffusion of ammonium ions, followed by internal diffusion of ammonium ions from a macroporous site to microporous site (36). A similar finding was observed from previous research, which adsorption of ammonium ions using coconut shell AC (36).

![Figure 11](a) Kinetic Pseudo-first order (b) Kinetic Pseudo-second order

Table 1. Kinetic study of TSAC

| Kinetic Study       | Parameters | Adsorbent |
|---------------------|------------|-----------|
| Pseudo-first order  | $q_{e,cal}$ (mg/g) | 1.008     |
|                     | $k_1$ (min$^{-1}$) | 0.003     |
|                     | $R^2$       | 0.7957    |
| Pseudo-second order | $q_{e,cal}$ (mg/g) | 1.737     |
|                     | $k_2$ (g/mg.min) | 0.028     |
|                     | $R^2$       | 0.9964    |
|                     | $q_{e,exp}$ (mg/g) | 1.858     |
Conclusions

It was proved that the activation process in the fabrication of TSAC shows an improvement in the characteristic of AC. Based on the parameters studied, the percentage yield of TSAC produced was 18.5%. The TSAC has a good pore development with 1372.51 m$^2$/g of surface area, 0.6756 cm$^3$/g of pore volume and 2.1453 nm of average pore radius, along with these characterizations, surface morphology and surface functional group of AC were also investigated. The batch adsorption experiment was conducted to study several factors, including the effect of contact time, temperature of solution and amount of dosage on adsorption of ammonium ions using TSAC. The $N_2$ adsorption/desorption isotherm shows a hysteresis loop with type IV isotherm, which indicates the presence of mesopores. It was observed that the 2 g of TSAC removed about 38% of ammonium ions after 20 h at an initial concentration of 50 mg/L, pH solution of 7 at 30°C. The optimum contact time required for the adsorption of ammonium ions onto TSAC was determined at 20 h. The adsorption of ammonium ions is favourable at a lower temperature. The adsorption of ammonium ions increased as the adsorbent dosage increased. The adsorption capacity of TSAC at equilibrium is 1.858 mg/g. The experimental data were fitted with Langmuir isotherm and followed Pseudo-second order.

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