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Effect of Activating Agents on the Adsorption of Ammoniacal Nitrogen using Activated Carbon Papaya Peel

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Ammoniacal nitrogen is one of the harmful pollutants in the waste water. High level of this pollutant can give a negative impact towards environment especially to aquatic life. Activated carbon has been known as an excellent adsorbent and widely used due to its large adsorption capacity. Papaya peel, a fruit waste, is a potential environmental friendly adsorbent. In this study, the efficiency of activated carbons from papaya peel to adsorb ammoniacal nitrogen by using different activating agents is investigated. The activated agents used are nitric acid (HNO_3), phosphoric acid (H_3PO_4), acetic acid ($C_2H_4O_2$), sodium hydroxide (NaOH), potassium hydroxide (KOH) and calcium chloride ($CaCl_2$). The purpose of chemical activating agents is to enhance the adsorption capacity and its removal efficiency. Maximum adsorption capacity (q_m) for ammoniacal nitrogen were determined by calculating the concentration of ammonium ion by using Nessler method (spectrophotometer, DR6000 Hach, US). The highest ammonium adsorbed was obtained from papaya peel activated with potassium hydroxide (KOH) with maximum adsorption capacity of 2.885 mg/g mass adsorbent used. The surface characterisation for the raw, after activation with potassium hydroxide and after adsorption was analysed by using Field Emission Scanning Electron Microscopy (FESEM) and the element analysis was conducted by using Energy-dispersive X-ray spectroscopy (EDX). FESEM morphology revealed that the activated carbons were found to be mainly micropores and mesopores. EDX revealed that nitrogen was the major component adsorbed by the activated carbon and it can be concluded that ammoniacal nitrogen has been adsorbed by the adsorbent. This result shows that papaya peel activated with KOH can effectively be used to remove ammoniacal nitrogen from the aqueous solution.

1. Introduction

Excessive release of ammoniacal nitrogen to the environment due to industrialisation and urbanisation causes a major crisis worldwide. Industries dealing with chemicals such as petrochemical, textile, electroplating and metal finishing contributes to ammoniacal nitrogen pollution and its release to the environment especially through wastewater discharges (Liang and Ni, 2009). Removal of ammoniacal nitrogen by using conventional method such as membrane filtration, chemical precipitation as well as biological method are not effective or economical as it gives lower percentage of removal. Use of adsorption process and agro waste derived material has shown very promising worldwide. Utilisation of such materials also has advantages like cheap price, readily available, low cost and simplicity to use (Hossain et al., 2012). The main contents in agriculture waste are hemicellulose, lignin, lipids proteins, simple sugar, water and hydrocarbon starch containing variety of functional group which shows the potential of ion binding capacity (Bailey et al., 1999). The unique and versatile nature of the activated carbon relates to their extended surface area, micro-porous structure and high degree of surface reactivity (Ismadji and Bhatia, 2001). Papaya peel, an agro-waste is discarded all over the world as useless material. According to Department of Agriculture Malaysia (DOA, 2013), Johor has the largest cultivation of papaya for the recent year (16,108.9 t). High consumption rate of papaya produces high

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amount of papaya peel waste causing waste management problems. By using it as alternative adsorbent, it can reduce the solid waste. Papaya peel has shown great potential as an alternative adsorbent to remove heavy metals such as chromium (IV) (Manjusha et al., 2012) and lead (II) (Abbaszadeh et al., 2016). The study by using papaya peel to remove ammoniacal nitrogen not been studied and is the main purpose of this study.

This present study focused on the preparation of the activated carbon using papaya peel and investigate the effect of six activating agents (nitic acid, acetic acid, phosphoric acid, potasssium hydroxide, calcium chloride and sodium hydroxide) on the removal efficiency of ammoniacal nitrogen from aqueous water. In addition, the surface morphlogy and element analysis will be analysed by using Field Emission Scanning Electron Microscopy (FESEM) coupled with Energy-dispersive X-ray spectroscopy (EDX). Surface area and pore size will be determined by using BET analyser.

2. Methods

2.1 Materials

Standard stock solution of ammonia chloride (1,000 mg/L) was prepared by dissolving 3.820 g solid ammonium chloride (NH_4Cl) in distilled water. The solutions with various concentrations was obtained by diluting the stock solution with distilled water (Liu et al., 2010a). In this study, chemicals such as 0.1 M nitric acid, HNO_3 (HMBG, 65 %), 0.1 M phosphoric acid, H_3PO_4 (MERCK, 99 %), and 0.1 M acetic acid, $C_2H_4O_2$ (HMBG, 99 %), 0.1 M sodium hydroxide, NaOH (MERCK, 99 %), 0.1 M Potassium hydroxide, KOH (HMBG, 85 %), and 0.1 M calcium chloride, $CaCl_2$ (QREC) were used to activate the surface of the papaya peel. For pH adjustment, 0.1 M Sulphuric acid, H_2SO_4 (PC) and NaOH were used. The equipments such as pH meter (Milwaukee MW102 PH, Germany), heating and drying oven (Constance, FCH 9036A, Germany), digital muffle furnace (Heattemp, Type S, Malaysia), waring blender (PanasonicMX 800S, Japan), digital orbital shaker Labwit ZHWY- 334, China) and weighing balance (Shimadzu ATX series, Japan) were used to conduct the experiments.

2.2 Preparation of Carica Papaya Activated Carbon (CPAC)

In this study, the peel powder of carica papaya fruit and its relative activated carbon was assessed as potential adsorbents to remove ammoniacal nitrogen from aqueous solution. The papaya was bought at the market and peeled. The peel was dried using oven for 24 h at 105 °C until they become crisp. Then the dried papaya was grinded until it becomes powder. This powdered was labelled as carica papaya raw (CP-raw). CP-raw was heated up to 400 °C in the furnace about 30 min to make relative charcoal and labelled as CP-char (Abbaszadeh et al., 2016). Then, 0.1 M acetic acid was used as activating agent in contact with CP-char for 2 d to modify the surface. After 48 h, the mixture was filtrate, and the filtered adsorbent was washed with chemicals either 1 % NaOH or 1 % H_2SO_4 followed by distilled water to make the adsorbent neutral and put in the furnace again for 2 h (Ahmida et al., 2015). After this process, the papaya peel sample is now called carica papaya activated carbon (CPAC). The dried CPAC was sieved to get 0.5 mm in size (using 500 micron mesh). The preparation of activated carbon was repeated with different activating agent by using the same concentration of 0.1 M of three different types of acid (nitric acid, phosphoric acid and acetic acid) and alkaline (sodium hydroxide, potassium hydroxide and calcium chloride).

2.3 Screening Test Using Different Activating Agents

The effect of activating agent as activating process by using acid and alkaline was investigated through several batch experiments to determine the highest adsorption capacity of ammoniacal nitrogen and percent removal for each activating agents. The batch experiment was conducted using parameter from literature review which are the optimum dosage of papaya peel adsorbentis 0.3 g (Li et al., 2012), time for the adsorbent and the solution (NH_4Cl) in contact is 2 h, initial concentration of ammonium chloride (NH_4Cl) is 50 mg/L and the pH is adjusted to pH 7 to make the solution in neutral condition according to Demirak et al. (2015). 0.1 M of three different types of acid (nitric acid, phosphoric acid and acetic acid) and alkaline (sodium hydroxide, potassium hydroxide and calcium chloride) were used and the highest results with high adsorption capa city and percent removal was chosen for further batch experiment in order to determine the optimum condition parameter for this study. The experiments were repeated at least with 3 samples for each acid/alkaline modification. The adsorbent was filtrated and the solution after filtration was analysed. Nessler method was used in order to determine the concentration of ammoniacal nitrogen after it has been adsorbed by carica papaya activated carbon (CPAC) using spectrophotometer (DR6000 Hach, US). The amount of adsorption q (mg/g) and the adsorption efficiency of ammoniacal nitrogen was calculated by using Eq(1) and Eq(2) (Hadi et al., 2011):

$$q\ (mg/g) = (C_o - C_i)\frac{V}{M} \quad (1)$$

$$\text{Percentage Removal (\%)} = \frac{C_o - C_i}{C_o} \times 100\ \% \quad (2)$$

Where C_0 (mg/L) is the initial liquid-phase concentration of ammoniacal nitrogen, C_i (mg/L) is the final concentration of ammoniacal nitrogen, V (L) is the volume of the solution and M (g) is mass of CPAC used.

2.4 Surface Characterisation

The surface morphology and microstructure of adsorbent were analysed using Field-Emission Scanning Electron Microscope (JSM-6701F, JEOL, Ltd) coupled with Energy Dispersive X-ray Analysis, EDX (S-3400N HITACHI), to identify the elemental composition of materials. For the sample preparation, sample is dried in the drying oven at 60 °C for at least 3 h or overnight. For biomass, it is necessary to coat the sample with conductor material such as gold, platinum or with carbon layer and this study use platinum as the coating material. This is due to the low electron conductivity of this material which will affect the images quality. The data generated by EDX consist of spectra showing the peaks corresponding to the element to give the composition of sample being analysed and its elemental mapping. The surface area and porosity of the raw papaya peel (CP-raw) and activated carbon papaya peel (CPAC) were evaluated using BET analyser instruments (Surfer Analyser, Thermo Fisher Scientific, Italy).

3. Results and Discussion

3.1 Carbonisation of Adsorbent

From the results in the Table 1, it clearly shows that, the carbonisation time has a significant effect on the percentage of carbon. The percentage of carbon increase with carbonisation time up to 30 min. This is because the composition in the papaya starts to change and convert into charcoal (carbon). From 30 min to 120 min of carbonisation time, the carbon percentage start to decrease, indicating that the longer carbonisation time will change the charcoal into the ash. According to study conducted by Gin et al. (2014), increasing the carbonisation time was found to reduce the quantity of carbonised product obtained from the peel due to excessive burning or oxidation and collapse the pore structure of the peels which was found to be predominate at long carbonisation time. Burning the peel within 30 min is chosen as the best carbonisation time and it will be used for further experiment.

Table 1: Elemental analysis of papaya peel after carbonisation process (CP-Char)

Sample	Time of Carbonisation (min)	Carbon, C (%)	Hydrogen, H (%)	Sulphur, S (%)
PP-raw	-	39.481	5.796	1.232
A	15	48.969	4.784	1.770
B	30	51.187	4.369	2.007
C	60	49.643	3.454	2.233
D	120	48.075	3.382	2.354

3.2 Effect of Activating Agent

The effect of chemical activation agents by using different activating agents are conducted by using batch experiments to determine the percentage removal and amount of adsorption capacity of ammoniacal nitrogen after the adsorption process. The result for percentage removal is illustrated in Figure 1. From Figure 1, the result shows negative results when sulphuric, acetic and nitric acid are used as activation agents. This may be due to some reactions occurring between acid and the solution that increases the concentration of ammonium ion after the adsorption process (Liu et al., 2010b). This indicates that acid is not suitable to be used as activating agent to remove ammoniacal nitrogen by using papaya peel. Positive results were seen when using alkaline (sodium hydroxide, potassium hydroxide, calcium chloride) as activating agents. Positive results show that, the concentration of ammoniacal nitrogen after the adsorption by using adsorbent modified with alkaline were lesser compared to before the adsorption takes place. The negative ion from alkaline makes the papaya peel ion more negative and this attracts and adsorbs more positive charge which are ammonium ion into the peel surface. Therefore alkaline are more suitable and chosen as activating agent to remove ammoniacal nitrogen. The mechanism of adsorption is shown in the Eq(3) and Eq(4) (Halim et al., 2013). The possibility to remove ammonium ion by using alkaline as activating agent on pine cone has been studied by Demirak et al. (2015). A study conducted by Boopathy et al. (2013), reveal that acid can also be used as activating agent to activate the coconut shell to remove ammonium ion. It can be concluded both acid and alkaline can be used as activating agents but it depends on the nature of the adsorbent and type of the adsorbate to be removed. Potassium hydroxide was chosen as the best activating agent in removal of ammoniacal nitrogen since it shows the highest percent removal compared to others. Through batch experiment, the highest removal percentage is 31.634 % with 4.593 mg/g ammonium adsorbed into the surface.

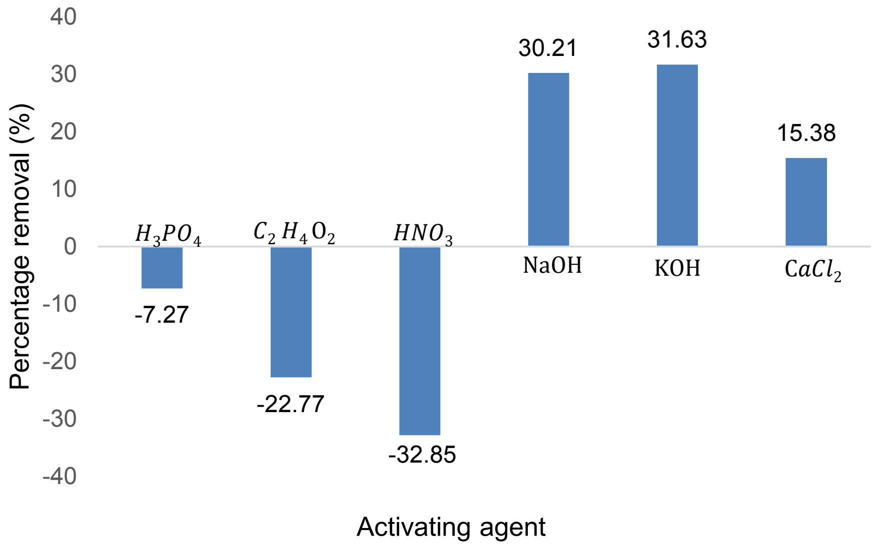


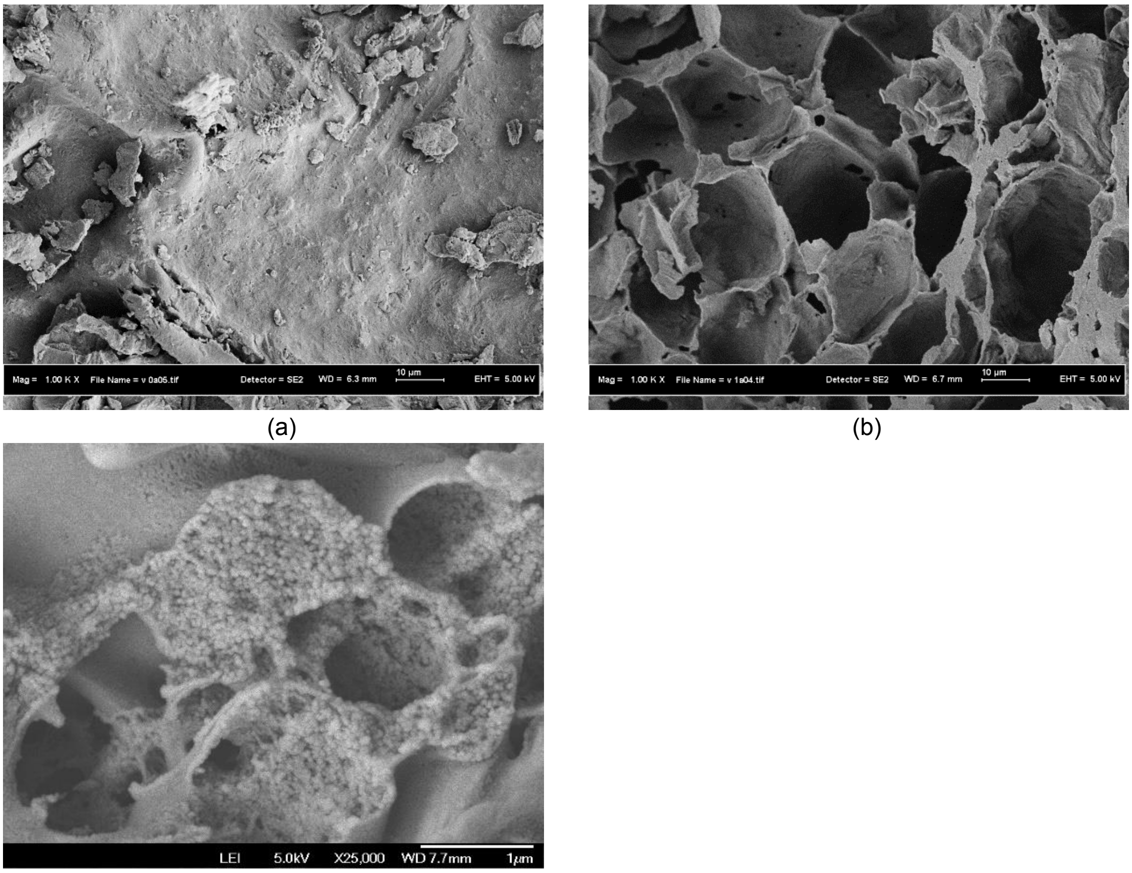
Figure 1: Removal efficiency and adsorption capacity of ammoniacal nitrogen

$$AC\text{-}R + KOH \longrightarrow AC\text{-}K + R + H_2O \quad (3)$$

$$AC\text{-}K + NH_4 \longrightarrow AC\text{-}NH_4 + K \quad (4)$$

3.3 Surface Characterisation

Surface characterisation were evaluated to compare the different characteristic of the new adsorbent after it has been modified and also after the adsorbent were used to adsorb Ammoniacal Nitrogen. The morphology and the nature of the surface structure for raw papaya peel, before and after adsorption are as presented on the FESEM image in Figure 2(a)-(c). Rough surface structure was seen for Figure 2(a) but then after the activated process, formation of pores can been seen (Figure 2(b)). The pores are covered with ammonium ion after the adsorption process (Figure 2(c)). The percentage of Nitrogen was confirmed through the elemental analysis by using EDX (Table 2) where the nitrogen percentage has increase by 43.35 % after the adsorption process and it is believed that it comes from ammonium ion. EDX mapping (Figure 3) is a mapping image to support the existance of nitrogen (diferent in colour) after the adsorption process. Through BET analysis, the surface area for raw papaya peel is 9.63 m^2/g and the surface area is increase after the peel is activated with KOH (26.559 m^2/g).

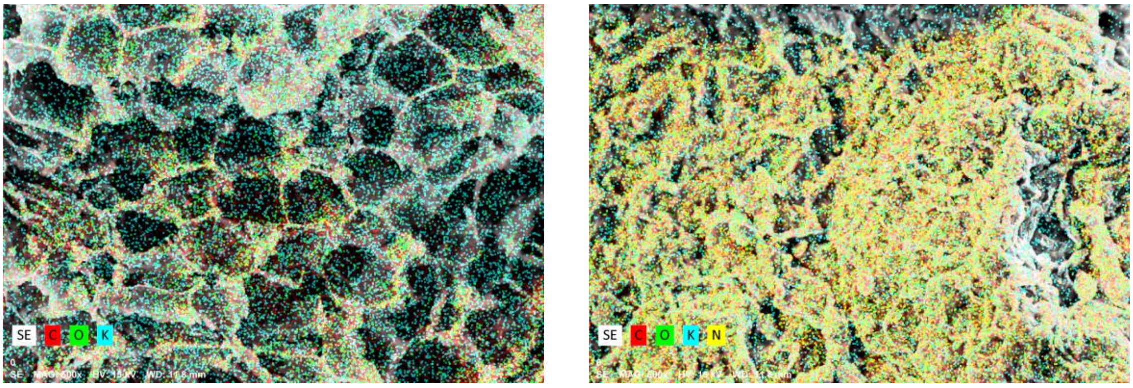


(a) (b) (c)

Figure 2: FESEM image for papaya peel powder. (a) Carica Papaya (CP) raw, (b) Carica Papaya Activated Carbon (CPAC) before adsorption of ammonium ion, (c) Carica Papaya Activated Carbon (CPAC) after adsorption of ammonium ion

Table 2: Elemental analysis before and after adsorption

	C (%)	O (%)	K (%)	N (%)	Surface Area (m^2/g)	Cumulative volume (cm^3/g)
Before Adsorption	65.23	28.20	6.57	-	26.559	0.0858
After Adsorption	59.95	23.46	0.52	16.07	18.685	0.0897



(a) (b)

Figure 3: EDX mapping for the CPAC (a) before adsorption and (b) after adsorption

4. Conclusion

This study has achieved the main objective which is to study the effect of activating agents on the adsorption of ammoniacal nitrogen and select the best activating agents to activate the papaya peel in order to remove ammoniacal nitrogen in the aqueous water. Based on the highest percent removal of ammoniacal nitrogen, potassium hydroxide shows the highest percent removal (31.63 %) and hence it has been chosen as the best activating agent to remove ammoniacal nitrogen.

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