

Effect of activation procedures on ammonia adsorption of bagasse fly ash from sugar industry waste

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Abstract. In this study, the effect of activation procedures on the ammonia adsorption of BFA was investigated. BFA was activated by chemical and physical methods, and the adsorption capacity and surface properties of BFA were analyzed. The results showed that both chemical and physical activation methods increased the BET surface area and porosity of BFA, which in turn enhanced its ammonia adsorption capacity. Specifically, chemically activated BFA performed the best, with a capacity of 5.34 mg/g. This study provides insights into the optimization of BFA as an adsorbent for ammonia and contributes to the development of sustainable and low-cost adsorption technologies.

1. Introduction

Ammonia pollution is a significant environmental concern due to its harmful effects on human health and ecosystems. It is a byproduct of various industrial and agricultural activities, such as fertilizer application, livestock production, and waste treatment [1]. Ammonia can contribute to the formation of fine particulate matter and nitrogen oxides, which can cause respiratory problems and cardiovascular diseases. In addition, ammonia deposition can lead to eutrophication, acidification, and biodiversity loss in terrestrial and aquatic ecosystems. To mitigate ammonia pollution, various technologies have been developed to capture and remove ammonia from air and water. Adsorption is one of the most promising methods due to its high efficiency, low cost, and easy operation. Activation is widely used process to enhance adsorption performance as it could develop surface area, porosity, and chemical stability of adsorbent. However, the source of adsorbents from non-renewable resources, such as coal and petroleum, raises environmental and economic concerns. Therefore, there is a growing interest in the utilization of renewable and low-cost materials as alternative adsorbent precursor for ammonia. Bagasse fly ash (BFA) is a waste material generated from the combustion of bagasse, a residue of sugarcane processing. BFA can be obtained at a low cost and in large quantities from sugar industries, which are abundant in Thailand where the annual sugarcane production was 92.03 million tonnes in 2021/22 [2]. Therefore, the utilization of BFA as an adsorbent for ammonia could provide economic and environmental benefits. However, the effectiveness of BFA as an adsorbent depends on the

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activation process, which could significantly affect its adsorption capacity. BFA could be activated by various methods, such as chemical activation and physical activation. Chemical activation involves the use of chemical agents, such as acids and bases, to create surface functional groups and micropores. Physical activation involves the use of high temperature and/or steam to create micropores and mesopores. Previous studies have reported the removal of cationic dye [3] and arsenic adsorption performance [4] of BFA under different activation conditions. However, the effect of activation procedures on the ammonia adsorption of BFA has not been fully understood. In this study, the effect of activation procedures on the ammonia adsorption of BFA was investigated to optimize the adsorption performance of this material. The specific objectives of this study were to (1) compare the ammonia adsorption capacity of BFA activated by different methods, and (2) characterize the surface properties and of BFA before and after activation. The findings of this study can provide insights into the optimization of BFA as an adsorbent for ammonia and contribute to the development of sustainable and low-cost adsorption technologies.

2. Methodology

2.1 Material

The bagasse fly ash (BFA) used in this study was obtained from Mitr Phol Bio-Power Co., Ltd. in Khon Kaen, Thailand. The BFA was washed with distilled water, dried, crushed, and sieved to a particle size range of 300 μm to 350 μm . Potassium hydroxide (KOH) and hydrochloric acid (HCl) of analytical grade were purchased from Sigma-Aldrich. Distilled deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$) was used to wash samples and prepare all solutions. In addition, nitrogen (N_2) and ammonia (NH_3) with a purity of $\geq 99.9\%$ and 99.5% , respectively, were used for the activation process and ammonia adsorption experiment. The synthesis of activated fly ash was achieved through a single-step physical or chemical activation process in a vertical tube reactor, as described in the previous work of Congsomjit et al. [5]. **Table 1** presents the proximate, ultimate and X-ray fluorescence (XRF) properties of the BFA in dry basis.

Table 1 The proximate, ultimate analysis and XRF result of BFA.

Item	Proximate Analysis	(%, dry basis)	Elemental analysis	(%, dry basis)	Inorganic composition	(%, dry basis)
BFA	Moisture	3.92	C	7.43	Al_2O_3	4.86
	Volatile matter	9.07	H	0.4	SiO_2	72.87
	Fixed carbon	3.51	N	0	CaO	5.85
	Ash content	83.5	O	16.1	Fe_2O_3	4.21
	-	-	Others	76.07	Others	12.21

2.2 Activated fly ash production

2.2.1 Physical activation

To carry out physical activation, 15g of crushed BFA were added to the reactor, and steam was used as the activation agent. Steam at a temperature of approximately 120 – 127°C was supplied directly to the reactor by a steam generator (Model 25X-2) during activation. Concurrently, nitrogen was delivered at a rate of 100 mL/min to prevent oxygen infiltration, which could cause combustion. The reactor was heated externally using a programmable digital PID controller from ambient temperature to 800°C at a heating rate of 5°C/min, with a holding time of 1 hour at the target temperature. The resulting product was washed with DI water to remove inorganic compounds formed during the activation process. The activated BFA product obtained from steam activation was designated as SFA. The activation equipment is shown in **Figure 1a**.

2.2.2 Chemical activation

Initially, 15g of powdered BFA was mixed with 2M KOH solution in the ratio of 1:2 at BFA to KOH weight. The mixture was stirred with constant speed rotation of 300 rpm for 2 h, centrifuged to separate liquid from mixture, and oven-dried overnight. The activation temperature, time, rate of nitrogen and heating rate were determined to be equal as physical activation mentioned in section 2.2.1 without using steam generator. The obtained activated fly ash was washed and neutralized with 1M HCl solution and DI water in order to eliminate KOH residues, and oven-dried at 105°C for 12 h. The chemically activated BFA was defined as CFA.

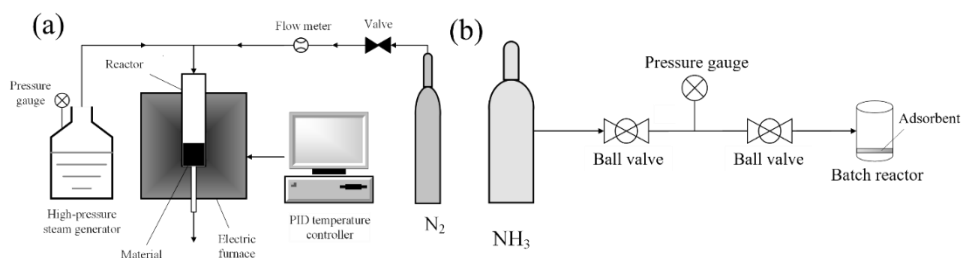


Figure 1. Diagram of (a) the activation procedure and (b) the ammonia adsorption test setup.

2.3 Characterizations

Proximate analysis of raw material was examined by LECO Thermogravimetric analyzer (TGA801). Ultimate analysis of BFA was conducted by Elemental Analyzer (Thermo Flash 2000). Brunauer-Emmett-Teller (BET) surface area, porosity and adsorption/desorption isotherm of samples were identified by Micromeritics ASAP 2020 surface and porosity analyzer. Elemental composition of materials was investigated by using XRF analysis (S8 TIGER Series 2). The surface morphology of material was investigated by Hitachi scanning electron microscope (SEM) Model SU8010. A batch adsorption experiment setup shown in **Figure 1b** was used to conduct the ammonia adsorption test. Initially, 1g of adsorbent was placed in a 21.2-ml reactor, and then ammonia was introduced from a gas cylinder tank into the reactor until the pressure of reactor went 2 bar. The gas feeding was then stopped by closing the ball valve once the pressure in the reactor reached the target pressure. The

pressure of reactor and time were observed from this point until the pressure was no longer reduced in 60 mins, indicating that the adsorption equilibrium was nearly reached, and the experiment was done. The NH₃ adsorption capacity was computed applying the ideal gas law, assuming that the pressure drop was proportional to the amount of NH₃ adsorbed into the adsorbent. The NH₃ adsorption capacity per unit of adsorbent (NH₃ adsorption capacity) was calculated using Equation 1.

$$\Delta n = \Delta PV/RT \quad (\text{Eq.1})$$

The change in the amount of NH₃ adsorbed by the adsorbent is represented by Δn , and is measured in millimoles (mmol). The pressure decrease detected in the batch reactor, measured in Pascals (Pa), is denoted by ΔP . The volume of the reactor is represented by V and measured in cubic centimeters (cm³). R is the standard international gas constant with a value of 8.31 J/mol·K. The adsorption temperature, denoted by T , is measured in Kelvin (K), and all tests were performed at room temperature. Each experiment was repeated at least three times in a random sequence to ensure the validity of the data. Before and after each experiment, leak tests were performed to confirm the experimental setup's integrity.

3. Results and discussion

3.1 BET surface area and porosity

The BET surface area and porosity parameters of FAs are presented in **Table 2**. It was clear that activation processes developed porosity of BFA since their BET surface area, micropore area and total pore volume were increased. The N₂ adsorption/desorption isotherms of BFA, SFA and CFA are shown in **Figure 2a**. All the samples performed type IV isotherms, indicating that they are microporous material. Besides, by the type H3 hysteresis loop, as classified by IUPAC were observed on three of them, suggesting that these materials are nonhomogeneous mesopores and/or micropores. It verified that even after activation, type of hysteresis loop and isotherms were still the same. The SEM images of BFA, SFA and CFA were exhibited in **Figure 3a-c** respectively. The porosity of SFA and CFA were developed after activation as several pores were formed throughout their surfaces. While, BFA showed lesser number of pores on its surface compared to CFA.

Table 2 BET surface area and porosity parameters of material.

Item	BET surface area (m ² /g)	T-plot micropore area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
BFA	39.76	22.54	0.029	2.95
SFA	46.76	19.46	0.041	3.72
CFA	51.92	35.06	0.043	3.13

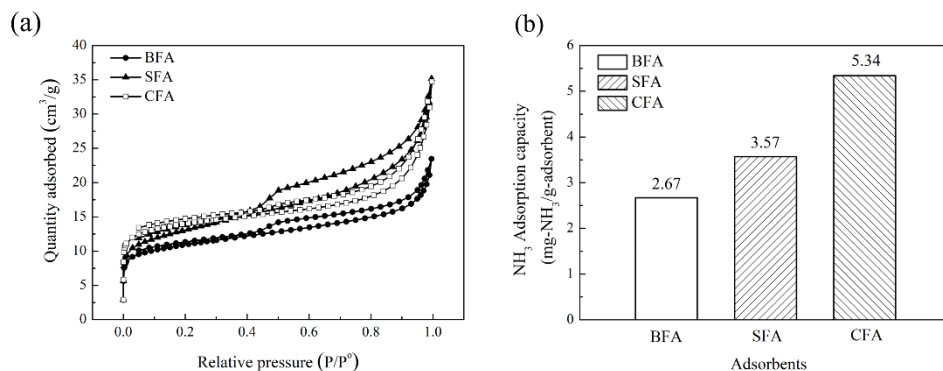


Figure 2 (a) N₂ adsorption/desorption isotherms, (b) NH₃ adsorption capacity of adsorbents, SEM image of (c) BFA and (d) CFA.

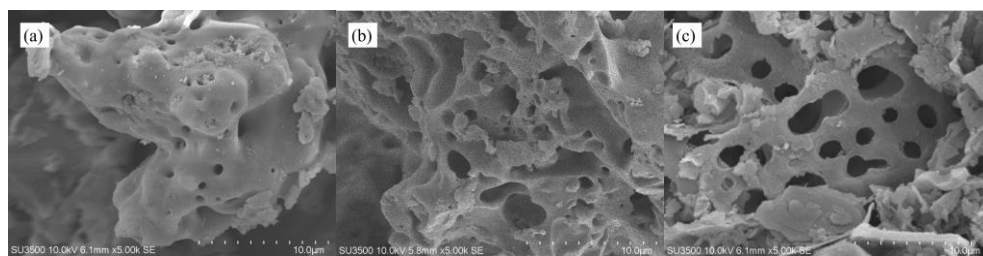


Figure 3 SEM images of (a) BFA, (b) SFA, and (d) CFA.

3.2 Ammonia adsorption capacity

The Ammonia adsorption capacity of BFA, SFA and CFA are shown in **Figure 2b**. As displayed, the amount of NH₃ per unit gram-adsorbent of BFA, SFA and CFA were 2.67, 3.57 and 5.34 mg, respectively. Activation methods like physical or chemical activation promoted a higher amount of adsorbed NH₃ along with greater BET surface area. Especially, CFA whose capacity was doubled from non-activated FA performed highest of 5.34 mg/g which was greater than that of SFA by 1.77 mg/g. The main reason is its surface functional groups such as hydroxyl, carboxyl, and amine groups can form chemical bonds with ammonia. Additionally, the alkaline nature of KOH can enhance the adsorption capacity of the fly ash for ammonia, as ammonia is a weak base and could be easily adsorbed by the surface functional groups that have acidic properties even if its BET surface area was slightly higher than that of SFA (46.76 vs. 51.92 m²/g).

4. Conclusions

In this study, the effect of activation procedures on the ammonia adsorption of bagasse fly ash (BFA) was investigated. The results showed that activation procedures significantly affected the ammonia adsorption capacity of BFA. Physical and chemical activation methods promoted a higher amount of adsorbed NH₃ along with greater BET surface area. Among the activated BFAs, chemically activated BFA (CFA) showed the highest NH₃ adsorption capacity of 5.34 mg/g, which was doubled from non-activated BFA. The enhanced adsorption capacity of CFA could be attributed to its surface functional groups, such as hydroxyl, carboxyl, and amine groups, which can form chemical bonds with ammonia. In addition, the

alkaline nature of KOH could enhance the adsorption capacity of CFA for ammonia. The findings of this study can provide insights into the optimization of BFA as an adsorbent for ammonia and contribute to the development of sustainable and low-cost adsorption technologies for ammonia removal.

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References

1. P. Jihoon, T. Kang, Y. Heo, K.Lee, K. Kim, K.Lee, C. Yoon, SH@W, **11**, 1(2020): 109-117.
2. Office of the Cane and Sugar Board. *Situation Report of Sugar Cane Plantation Production Year 2021/22*. (2022)
3. A. Chumpiboon, K. Thongsubsai, T. Pongsiri, J. Knijnenburg, Y. Ngernyen, EASR, **49**, 3(2022): 381-394.
4. S. Suresh, M. Sillanpää, F. Banat, R. Vissa, J Environ Health Sci Eng, **20**, (2022): 1-19.
5. D. Congsomjit, C. Areeprasert, Biomass Convers. Biorefin., **11**, (2021): 2569-2584.
6. T. Ketwong, R. Doong, C. Areeprasert,. *IOP Conference Series: Earth and Environmental Science: IOP Publishing*, (2021):012006.