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Performance of CO_2 Adsorption on Modified Activated Carbons Derived from Okara Powder Waste: Impacts of Ammonia Impregnation

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Abstract: The activated carbons (ACs) derived from okara powder waste with high surface areas were modified with ammonia aqueous solution impregnation in an autoclave to enhance their CO_2 adsorption properties toward CO_2. The impregnated ACs were characterized in which surface chemical composition and properties of the ACs were analyzed by SEM-EDX, FTIR. Activated carbons were functionalized with ammonia aqueous solution (25%) through a hydrothermal process within 24; 48, and 72 hours. The adsorption performance of CO_2 onto carbon samples was experimentally evaluated through a TPD CO_2 measurement. FTIR spectra confirm the N-containing in N-modified activated carbons and the presence of the $-C = O$ stretch and N-H groups. CO_2 uptakes of N-modified activated carbons are 0.24; 1.47; and 1.20 mmol/g, which are relatively comparable with those of activated carbons studied in in the literature.

Keywords: activated carbon; adsorption; biomaterials; functional groups; surface areas; hydrothermal process; chemical composition; biomass

1. Introduction

Carbon dioxide (CO_2) emissions are causing anthropogenic climate change or global warming which is a challenge for human beings in this century and needs to be addressed [1–5]. Among technological approaches, adsorption technologies by using solid adsorbents which include natural calcium materials [6], MOFs, zeolites, and activated carbons [7,8], have been considered as promising solutions to mitigate CO_2 due to their low energy requirement, simplicity, cost-effectiveness, and scalability [9,10]. Of the solid adsorbents, activated carbons synthesized from biomass with high surface areas are gaining attention for their low cost, high surface area, high porosity, and large-scale application potentials [11,12].

Basic groups (amine groups) are known to enhance the structural, alkalinity, and chemical properties and adsorption efficiency [9,10,13] of activated carbons [14]. Amine groups can be increased onto the activated carbons by wet [14] or dry or dry impregnation methods, depending on whether aqueous or gaseous NH_3 was injected into activated carbons at different temperatures [10,15]. The thermal modification using NH_3 is normally known as amination and the temperature ranges are normally from 200 °C to 800 °C [15]. Through the heating process, NH_3 disbands to various free radicals such as NH_2, NH, atomic H_2, and N_2. These free radicals will then react with carbons to produce N-functionalities such as -CN, pyridinic, and pyrrolic [15]. When ammonia impregnation is applied, it is expected that the amount of incorporated N_2 will be improved on the activated carbons [16], this leads to also to enhance the CO_2 adsorption capacity [9,10,13], since CO_2 is acidic. For instance, Zhang [9] used microwave irradiation under N_2 atmosphere and NH_4OH impregnation to increase the CO_2 adsorption up to 3.75 mmol/g at 1 atm and 20 °C [9]. Ava Heidari [13] used ammonia solution with heat modification to achieve the CO_2 adsorption capacity of up to 3.22 mmol/g at 1 bar

and 30 ^{o}C [13]. However, impregnating activated carbons into a basic solution or through the wet impregnation process might result in blocking pores in the structures of activated carbons [16] and lead to the adsorption decrease [9].

Okara powder waste, often considered food-processing waste [17] and discarded or underutilized during soy-bean production processes, represents an environmentally friendly feedstock for activated carbon production by fast pyrolysis processes [18,19]. The hydrothermal process has been known as a simple method to improve activated carbon adsorption properties [19–21]. This research aims to evaluate the impacts of ammonia aqueous solution impregnation through hydrothermal treatment at 200 ^{o}C on relatively high surface area okara powder waste activated carbons toward CO_2 adsorption capacity. The textural structures of the modified ACs derived from okara powder waste were characterized. The functional groups and composition of elements of the ACs were further analyzed by Fourier transform infrared spectroscopy (FTIR). The adsorption of CO_2 on the original and modified ACs was measured, discussed, and reported in this study. By investigating this bio-waste material, the research not only addresses sustainability issues but also contributes to waste valorization [22].

2. Materials and Methods

2.1. Materials and Instruments

Original activated carbons were prepared from pyrolysis processes with dry KOH (Xilong, China) activation. The high surface area (590 m^2/g) [18] was obtained from a two-step carbonization and activation method. First, okara powder waste was sun-dried and oven-dried before it went through a vertical and horizontal pyrolysis setup in a N_2 flow of 1.8 L/min to obtain the biochar. Pyrolysis temperature is set at 550 ^{o}C; heating rate 3 ^{o}C/min; residence time is 1 hour; in a N_2 flow of 1.8 L/min. After that, the biochar was impregnated with dry KOH and went through washing and re-pyrolysis steps with pyrolysis temperature set at 550 ^{o}C; heating rate 3 ^{o}C/min; residence time: 1 hour before testing their BET surface area values. These steps were described in detail in a previous study [18].

2.2. Modification of ACs

The original activated carbons have surface areas of 590 m^2/g and were divided into 4 samples where sample 1 (denoted S1-original AC) remains the original activated carbon with high surface areas. Prior to the surface modification, the AC was dried in an oven (Nabertherm, Germany) at 100 ^{o}C for 24 hours and kept in a zip bag. Sample 2 (denoted sample S2-AC-NH$_4$OH-24h) was impregnated with NH_3 solution 25% (Xilong, China) in an autoclave and kept in an oven (Nabertherm, Germany) at 200 ^{o}C for 24 hours. 75 ml ammonia aqueous solution (25%, Xilong) was added to 0.5 g of the original AC, the heating rate is 3 ^{o}C/min. Sample 3 (denoted as S3-AC-NH$_4$OH-48h) and sample 4 (denoted as S4-AC-NH$_4$OH-72h) were activated carbons with NH_3 solution 25% (Xilong, China) impregnated in an oven (Nabertherm, Germany) at 200 ^{o}C for 48 and 72 hours, respectively.

2.3. SEM-EDX

A Jeol, JCM-7000 microscope (Tokyo, Japan) was used to perform the scanning electron microscopy (SEM) images of the samples. SEM images were captured at 3000 magnification. EDX analyses were examined with a 10 kV acceleration voltage by the same instrument.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The surface FTIR spectra were taken with a Thermal Scientific – NICONET iS5050 FTIR (USA) instrument. The samples were dried in a vacuum desiccator (Jeio, Korea) before being mixed with KBr powder and pressed with a Specac hydraulic press (England). Data acquisition was obtained automatically from the standard software package installed in a connected computer. The samples

were run after a pure KBr sample known as a baseline result. The spectrometer collected 1800 spectra in the range of 400–4000 cm^{-1}, with a resolution of 2 cm^{-1}.

2.5. Temperature Programmed Desorption of CO_2 on ACs

TPD is a useful technique to characterize adsorbed species, to find acidic and basic sites on the surface, chemically bonded surface, or organic compound adsorbed on the surface of the sample [23,24]. TPD coupled to mass spectrometry(MS) instrument was provided by Micrometrics, AUTOCHEM – 2950 (GA 30093, USA). The experiments were carried out in a TPD cell placed into a stainless steel, cylindrical heating block. 100 mg of the sample was placed in a quartz reactor. The degassing process takes place within 15 min with Helium (99.99%) flow at 300 °C; heating rate of 3 °C/min and then the sample was then cooled to 50 °C s for CO_2 chemisorption in 10% CO_2/helium. Then the TPD-CO_2 temperature is increased up to 500 °C; heating rate of 10 °C/min and keep this temperature in 30 min for desorption [23,25,26].

3. Results and Discussions

3.1. Impact on Morphology and Composition of Activated Carbons

SEM photographs of the original activated carbon and modified samples are shown in Figure 2. It is observed from the figure that the external surface of all activated carbon samples shows some pores. Visually, the carbon samples present similar structures but the ammonia modifications also caused changes to the surface morphology. Changes can be seen in Figure 2 (b, c, d) that the thick wall becomes opened; porosity gets wider; and SEM images in (b), and (c) have more pores and channels than the raw/original activated carbon (a) [27] and the surface of sample (d) looks smoother [28].
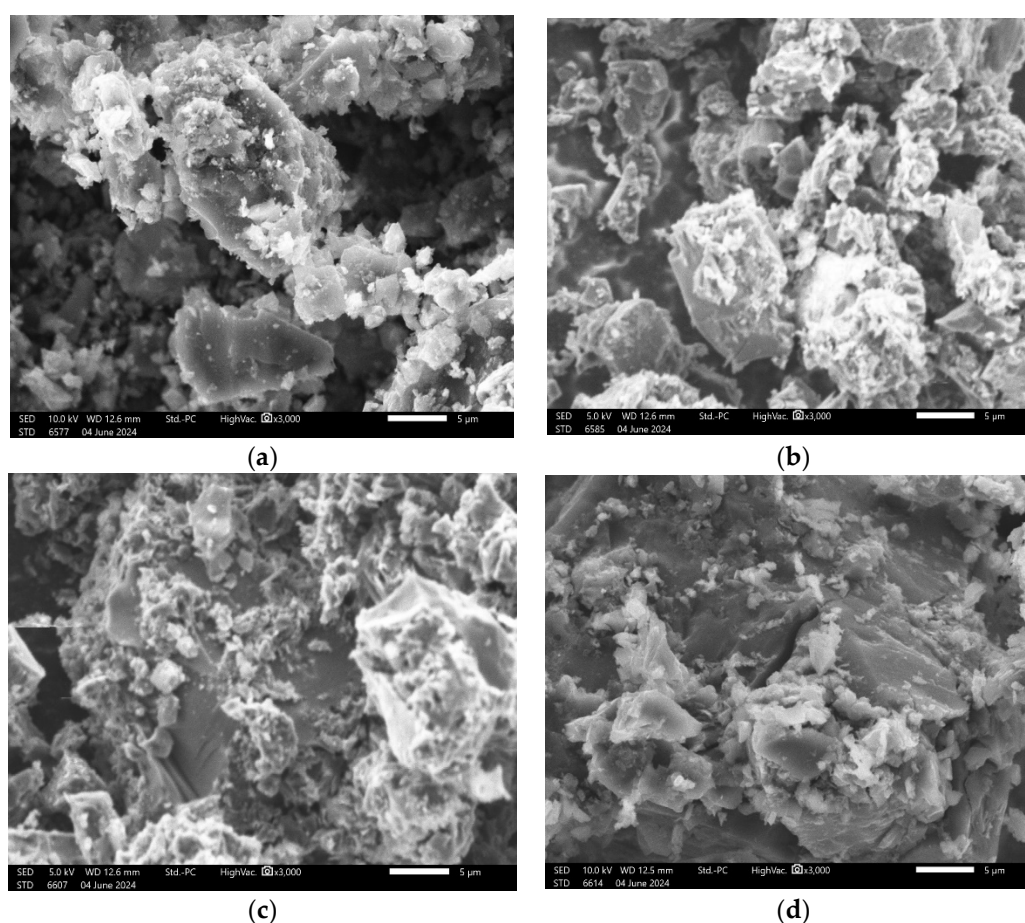

Figure 2. SEM images of samples (a) S1-original AC, (b) S2 –AC-NH$_4$OH-24h, (c) S3-ACNH$_4$OH - 48 h (d) S4 -NH$_4$OH - 72h.

From Table 1, we can see that there is no N in the raw AC sample. For samples S2 S3 and S4, with an increase in hydrothermal time, the N concentration in the mass of those samples are 4.34; 6.05; 1.58 (%), while the N concentration in the atom is 4.17; 5.70, and 1.16, respectively. The C/N atom ratio clearly shows that the AC modified with NH_4OH for 48h (S3) possesses the highest N content. The decrease in N concentration in sample S4 (when hydrothermal duration is 72 hours) can be due to the NH_3 desorption from pores in this sample in a too-long heating treatment process. Thus, samples S2 and S3 with a reasonable heating time (24h and 48h) may have better CO_2 adsorption ability due to higher N content. Of these 4 samples, Cl only appears in the original AC, this is possible because the Cl impurities remain from the washing step using aqueous HCl solutions of the AC preparation steps [18].

Table 1. Chemical composition of different samples S1-S4.

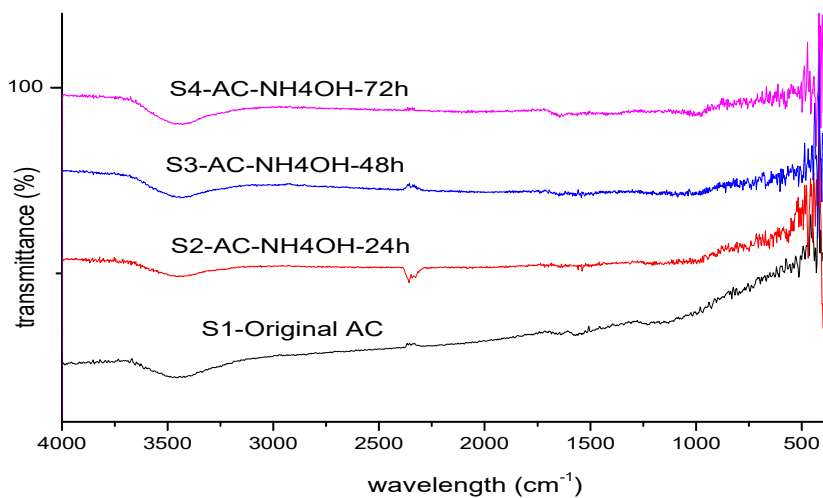| Elements	S1 (Original AC)		S2 (AC-NH₄OH-24h)		S3 (AC-NH₄OH-48h)		S4 (AC-NH₄OH-72h)	
	Mass%	Atom%	Mass%	Atom %	Mass%	Atom%	Mass%	Atom%
C	88.39	95.63	66.64	74.57	71.25	78.29	71.30	87.74
Al	1.16	0.56	2.08	1.04	0.97	0.47	2.06	1.13
Si	1.81	0.84	3.23	1.55				
Cl	3.05	1.12						
K	5.59	1.86	2.48	0.85	4.90	1.65	25.07	9.48
N			4.34	4.17	6.05	5.70	1.58	1.16
O			21.22	17.83	16.82	13.88		
Total	100	100	100	100	100	100	100	100
C/N atom ratio		0		17.88		13.74		75.63

EDX results of sample S2 are illustrated in Figure 3. The result shows that this sample has the highest oxygenated groups compared to other samples (S1, S3, and S4). This sample also contains a Si concentration of 3.23% in mass and 1.55% in atoms, which is relatively high compared to the literature of between 0.09 and 1.21 % [18,29].
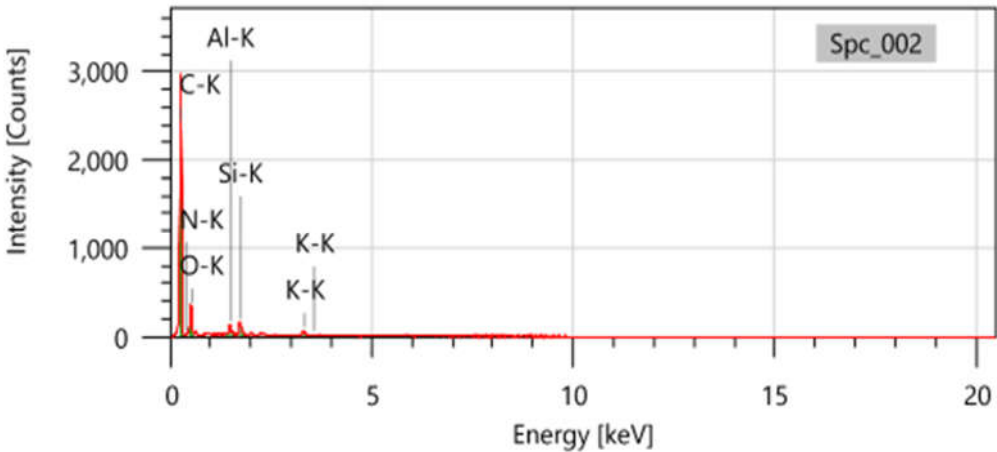
Figure 3. EDX spectra of sample S2.

3.2. Impact on Functional Group of Activated Carbons

Functional groups and complexes inside the samples were analyzed through infrared-spectra analysis. FTIR spectra of these 4 samples are shown in Figure 4.

Figure 4. FTIR spectra of S1 -Original AC, S2 -AC-NH4OH-24, S3-AC-NH4OH-24 and S4-AC-NH4OH-72.

Visually, FTIR analysis results of 4 investigated samples show quite similar spectra. Around the wavelength of 2358 cm^{-1}, corresponding to the $-C = O$ stretch [30,31], a small peak appears at samples S1-Original AC, S3 -AC-NH4OH-24 and S4-AC-NH4OH-72. The FTIR spectra confirm the presence of N-containing groups in ammonia-modified activated carbons (samples S2 -AC-NH4OH-24, S3-AC-NH4OH-24, and S4-AC-NH4OH-72). The characteristic band at the wavelength of 3432cm^{-1} and 3442 cm^{-1} of both treated and untreated AC spectra shown could be due to the $-OH$ asymmetric stretching vibration or the presence of N-H groups [18,32,33].

3.3. Impact on CO₂ Adsorption Ability

CO$_2$ adsorption experiments through the break-through apparatus were carried out with samples S1-S4. The CO$_2$ uptake capacity of these samples was compared with previous studies as illustrated in Table 2.

**Table 2.** Comparison of CO$_2$ adsorption data with those of other research in the literature.

Adsorbents	Sample code	Temperature (K)	Impregnation method and agent	CO₂ uptake (mmol/g)	References
Okara	S4-AC-NH4OH-72h	298	Chemical, wet, NH4OH	-	This work
Okara	S1-Original/raw or unmodified AC	298	Chemical, wet, NH4OH	0.24	This work
Crystallized materials	ZIF-100	298	-	1.05	[34]
Okara	S3-AC-NH4OH-48h	298	Chemical, wet, NH4OH	2.24	This work
Okara	S2-AC-NH4OH-24h	298	Chemical, wet, NH4OH	1.78	This work
Commercial AC	Norit RB2	298	-	1.5	[35]
Zeolite-based adsorbents	13X	298	-	2.27	[11]
Commercial ACs	Commercial ACs	298	Chemical, wet, NH4OH	2.92	[9]

Coffee Grounds	-	298	Chemical, wet, KOH	3.00	[36]
Eucalyptus wood	-	298	Chemical, H_3PO_4	3.22	[13]
Rice Husk Char	-	298	Chemical, wet, KOH	3.71	[37]
Carrot Peels	-	298	Chemical, wet, KOH	4.18	[38]
Celtuce Leaves	-	298	Chemical, wet, KOH	4.36	[39]
Peanut Shell Char	-	298	Chemical, wet, KOH	4.41	[40]
MOF	Mg-MOF-74	298	-	5.77	[11]

In this work, CO_2 uptake capacity was calculated from the desorbed CO_2 amount in the TPD CO_2 measurement. The results exhibit a strong difference between the S1-original AC sample compared with the S2-AC-NH_4OH-24h, S3-AC-NH_4OH-48h, and with the cited literature research. Specifically, S1-original AC has much lower CO2 uptake compared to S2-AC-NH_4OH-24h, and S3-AC-NH_4OH-48h since these samples have been modified with NH groups. As the content of N is highest in the S3 sample as described in EDS results, this sample also has the highest CO_2 uptake, which is a reasonable value compared to the CO_2 uptake reported by other researchers in the literature. Thus, it can be concluded that the treatment with NH_4OH for 48h is optimal for the modification of Acs to adsorb CO_2.

3.4. CO_2 Temperature-Programmed Desorption (CO_2-TPD) experimental results

The CO_2-TPD experimental results are shown in Figure 5. From the TPD profiles, the S1-original AC has its peak in the low-temperature region (50 – 180°C) while the S2-AC-NH_4OH-24h and the S3-AC-NH_4OH-48h has its peak in the high-temperature region (290 – 500°C), representing that the original AC only weakly adsorb CO_2 while the modified samples strongly adsorb CO_2 so that they release CO_2 at high temperatures [41]. Figure 5 shows that when the adsorption temperatures increased, the intensity of the peaks rose reaching the highest values at 400 °C, which is in good agreement with the literature [42]. The CO_2- TPD for sample S1 - original AC implies at the temperature reaches 97 °C, that there was a small amount of released CO_2. For samples S2 – AC-NH_4-24h and S3-AC-NH_4OH-48 h, when the temperature gets 400 °C, there is a significant amount of released CO_2 possibly because of the desorption of CO_2 and the decomposition of other functional groups inside the samples [28,43,44]. The release of CO_2 below 400 °C indicates that there are carboxylic groups prensented in the surface of the different activated carbon samples [28].
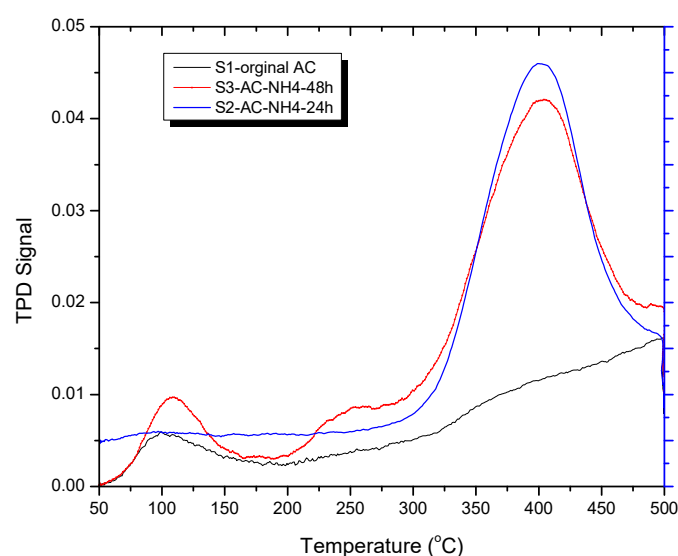
Figure 5. TPD-CO_2 spectra for samples S1-Original-AC, S2-AC-NH4OH-24 h and S3-AC-NH4OH-48 h.

The masses of the released CO_2 and NH_3 were monitored during the TPD CO_2 measurement, according to the method described in the literature [43]. The results of mass 44 for CO_2 are shown in Figure 6. The changes of mass intensity with temperatures fit quite well with the TPD CO_2 profiles in the high-temperature range of the samples, showing the fact that CO_2 was released at high temperatures from $220 – 475^oC$. Besides, the mass 17 of NH_3 of sample S3 was also examined as shown in Figure 7 to see if NH_3 functionalized in AC materials is also released during the increase of the temperature. Here the signals were also observed at low-temperature regions and thus fit with the TPD CO_2 profile of the samples. Therefore, the released NH_3 contributes to the peaks at low temperatures $(50 – 175^oC)$ in the TPD CO_2 profile of the S3 sample. NH_3 was also released at high temperatures. Thus, the modification of ACs by NH_4OH solution only resulted in a weak bond with AC.
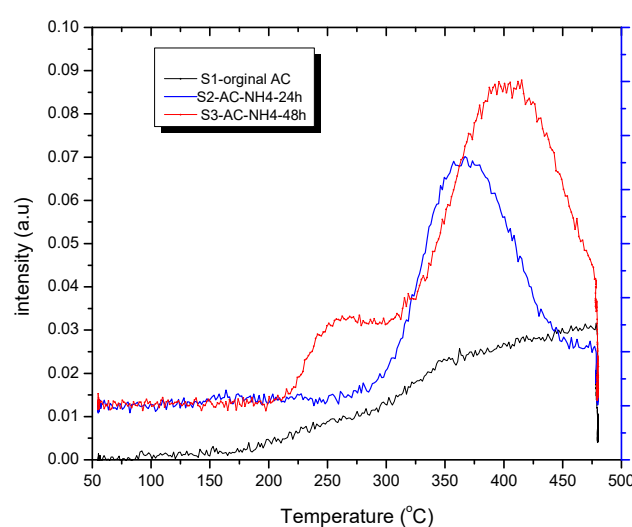
Figure 6. Mass intensity of mass 44 (CO_2) for samples S1-Original AC, S2-AC-NH4OH-24 h, and S3-AC-NH4OH-48 h.
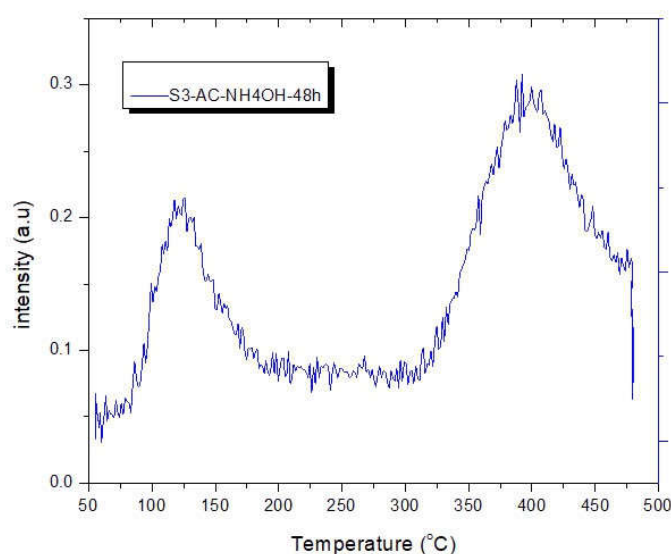
Figure 7. The mass intensity of mass 17 (NH_3) for sample S3-AC-NH4OH-48 h.

4. Conclusions and Outlooks

Activated carbons (ACs) were derived from okara powder waste and activated by KOH for CO_2 adsorption. The surface of ACs was impregnated with ammonia aqueous solution using a hydrothermal process at 200 °C to enhance the CO_2 adsorption. The prepared activated carbon samples were characterized with SEM-EDX and FTIR. Ammonia impregnation improved the morphology of the activated carbons. The amounts of the basic groups on the carbon surfaces became more. The performance of CO_2 uptake onto okara-based activated carbons was evaluated at different hydrothermal durations. The amount of CO_2 adsorbed onto ACs increased when the hydrothermal and impregnation time increased. The findings have implications for advancing carbon capture technologies [5] and promoting the use of agricultural byproducts [22].

Looking forward, several new approaches can be researched to further advance this study. First, investigating a broader range of ammonia impregnation conditions such as dry ammonia impregnation and activation processes could give additional optimizations for CO_2 uptake capacity. Additionally, investigating the adsorption isotherm simulation computational modeling might give new insights into the CO_2 uptake mechanisms and capacity. Combining ammonia impregnation with other modification strategies, such as doping with additional heteroatoms or integrating advanced material composites, may further enhance CO_2 adsorption properties. Expanding the research to various other feedstocks for activated carbon production and comparing their performance may provide a more comprehensive understanding of the material's adsorption performance.

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