

## NaOH/Microwave-Assisted Synthesis of Carbonate-Rich Activated Charcoal for Catalytic Oxidation of Nitrite in Aqueous Solution

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**Abstract:** Activated charcoals were prepared by activation with 600 W microwave irradiation in combination with pretreatments of tamarind wood derived charcoal in boiling mixtures with NaOH (1 g : 0 g - 1 g: 0.12 g). The samples were characterized by FTIR, XRD, SEM-EDS, and BET, and used for catalytic nitrite oxidation under air atmosphere in the absence of light at 30 °C, pH 6.5, and 120 rpm shaking for improved efficiency. The results show that the percent yields of tamarind wood derived activated charcoals (ACCs) were 88.51% - 94.66 %. The main carbonate compounds of ACCs are present in the materials after activation. Na<sup>+</sup> ions and water molecules could be inserted into the graphitic layers during pretreatment and efficiently effected surface cracking of ACCs by 600 W microwave irradiation. The surface cracklings and porosities of ACCs increased with increasing concentration of NaOH from 1 M to 3 M with optimum at 2 M NaOH. The final products are mesopore materials containing macro and meso hole channels. It was found that the nitrite conversions exhibit high reaction rates within 20 min. The reactions proceed via catalytic oxidations, and their rates increase with increasing concentrations of NaOH activation, while nitrite conversions via the disproportionation reaction were inhibited. The optimized catalyst with 1 g : 0.08 g activation ratio enhanced the oxidation conversion by up to 16-fold compared to the catalyst-free system. In addition, spent ACCs with 1 g : 0.04 g - 1 g: 0.12 g activation ratios remained stable and exhibited catalytic oxidation activity after three catalytic cycles with oxidation conversion efficiency consistently falling in the range of 32.22%-49.48%.

*Keywords: Microwave irradiation, Sodium hydroxide, Activated charcoal, Catalytic oxidation, Nitrite*

## 1. INTRODUCTION

Nitrite is usually found in aquatic environments and originates from fertilizer uses, manure applications, and sewage discharge. It is a human carcinogen and can cause methemoglobinemia [1]. Therefore, it is necessary to eliminate nitrite present in wastewater. The most widely used methods used in the past were catalytic reduction,  $\gamma$ -ray irradiation, and ion exchange, but these are expensive, relatively slow, and complex [2, 3]. Nitrite can be both reduced and oxidized via a disproportionation reaction, which transforms it from its oxidation state of +3 to the oxidation state of +2 in nitric oxide and the oxidation state of +5 in nitrate, under ambient conditions in natural environments [1]. On the other hand, nitrite oxidation reaction, which involves the addition of an oxygen atom to the nitrite ion and produces only nitrate ion, is also possible. However, there is very little research reported for the nitrite oxidation reaction, especially catalytic oxidation. Normally, the competitive relationship between oxidation and disproportionation reaction pathways in the liquid phase ultimately suppress  $\text{NO}_2^-$  oxidation efficiency [2]. The disproportionation is an undesirable side reaction, which releases NO gas causing secondary pollution, while oxidation reaction produces only nitrate ions, which are more stable and cause less pollution [4]. Therefore, the use of the oxidation reaction for nitrite conversion to nitrate is desirable for environmental water treatment. Nitrite oxidation reactions include the nitrification process by nitrite oxidoreductases from nitrite-oxidizing bacteria, chemical oxidation by an oxidizing agent [eg.  $\text{CeO}_2$ ,  $\text{MnO}_2$ ], and metal oxide doped catalysts [2, 4]. The photocatalysis by semiconducting materials [5, 6] and electrocatalysts in the form of suspension, immobilized layer on the surface of an electrode, or immobilized on any other inert material [3, 5] is also used for nitrite conversion by catalytic oxidation. However, nitrite is highly soluble in water and has a low affinity for most natural sorbents, and thus it is mobile and persistent in the environment [1]. In addition, achieving nitrite removal via nitrification would be time-consuming [2]. This problem could be solved by adsorbent materials, which could immobilize

nitrite for enhanced oxidation reaction via surface catalytic transformation. Catalytic oxidation on the surface of a catalytic adsorber involves oxygen molecules from the air reacting with nitrite ions on the surface of the catalysts to form nitrate [7]. On the other hand, the disproportionation reaction involves the nitrite ions transforming internally into both nitrate and a lower oxidation state nitrogen compound [1]. However, the disproportionation reaction could be inhibited by  $\text{pH} > 5$  [8], anionic surfactants (sodium dodecyl benzene sulfonate and sodium dodecyl sulfonate in aerobic denitrification) [9], metal-oxide electrocatalysts (NiCo oxide composite) [10], and scavenger intermediates (eg. polymerization, free radicals) [11]. On the other hand, some catalysts have been used for nitrite oxidation conversion to nitrate such as zeolites, metal exchanged zeolites, carbon materials, metal oxides, and metal-based catalysts [2]. The atmospheric conditions, which have been used for nitrite oxidation, are pure oxygen [8], ozone [2, 12], and air [6]. Hydrogen peroxide has also been used for the oxidation of ammonia to nitrite and subsequently to nitrate [13]. However, there is very little reported research for the nitrite oxidation reaction, especially using carbon-based materials for catalytic oxidation. There are some reports that have described the use of zeolites [8], Mn-zeolites, aluminosilicates [2], and  $\text{TiO}_2$  nanoparticle-acrylic [6] for nitrite catalytic oxidation under  $\text{pH} 3-4$  with oxygen, oxygen-ozone, ozone, or air atmosphere. Undesired disproportionation reactions were also observed in these reports. Therefore, this research is focused on the preparation of activated charcoal to be used for nitrite conversion into nitrate via surface catalytic oxidation under mild conditions without disproportionation reaction. In general, activated carbons have been produced by physical activation by oxidizing gases like steam, air, and  $\text{CO}_2$ , and by chemical activation with dehydrating chemical agents including phosphoric acid, sulfuric acid, potassium hydroxide, and zinc chloride, at high temperatures and under inert atmosphere [14]. NaOH is an oxidizing chemical agent, which is used for the preparation of activated carbon materials by causing dehydration, oxidation, and reduction reactions that erode the carbon structure and create pores, resulting in a high-surface-area materials with excellent adsorption properties [15]. In this research, NaOH was used for chemical activation along with microwave irradiation for the preparation of activated charcoal. It is expected that the final products will have a basic character inhibiting the disproportionation reaction.

Moreover, microwave irradiation co-activation may reduce the activation reaction time. It was reported that thermal plasma treatment by microwave power of 800 W for activated carbon preparation could induce disordered structure along with the decrease of oxygen on the surface within 5 min of irradiation time [16]. Activated carbon products with abundant surface hydroxyl species, which are prepared by microwave irradiation and sodium hydroxide, had been used for desulfurization of coal with high efficiency [17]. This method was also used for the activation of sawdust, which produced mesoporous structured activated carbon that resulted in demolished cellulose and hemicelluloses, lignin solubilization, and swelling of biomass samples [18]. In the same way, activated carbon products made from biodiesel industry solid residues are mainly macro and mesoporous materials [19]. It was shown that porous activated carbons made using NaOH along with microwave irradiation depended on the types of raw materials. However, the use of simple, carbonate-containing, NaOH/microwave-activated charcoal for the selective catalytic oxidation of nitrite under mild, ambient air conditions has not been reported.

The objective of this research was to study the effects of NaOH concentration and 600 W microwave irradiation power on the activation of tamarind wood charcoal. The physical and chemical characteristics of the final products were investigated by FTIR, FESEM-EDS, and BET analysis. Finally, nitrite catalytic oxidation conversion into final products was investigated under conditions close to the natural environment.

## **2. MATERIALS AND METHODS**

### **2.1 Activated Charcoal Preparation**

Tamarind wood derived charcoal (CC) was prepared using carbonization at around 500°C and was obtained from a local traditional kiln at Bankrang district, Phitsanulok province, Thailand, was ground and screened by 60 mesh sieves (Laboratory test sieve, Retsch, Germany). The powder CC was dried in an oven (SL 1375 SHEL LAB 1350FX) at 105°C for 3 h. Samples of the dried CC powders (20 g, weighed

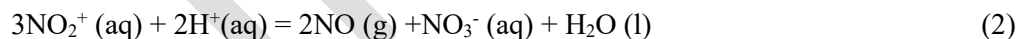
by Sartorius ED224s, Germany) were impregnated with 0 M – 3 M NaOH (reagent grade, Merck, Germany) solution with a ratio of 1:1 of CC weight to NaOH volume (calculated as weight charcoal per weight NaOH = 1 g : 0 g, 1 g : 0.04 g, 1 g : 0.08 g and 1 g : 0.12 g). The samples were pretreated by boiling at 100°C for 1 h. After that, the samples were microwave irradiated with 600 watts (SAMSUNG ME711K, 20 L, Bangkok, Thailand) for 15 mins in the absence of inert gas, following the report of Liew et al. [20], to provide no excessive heat energy for pore development. The final product powders were dried at 100°C in an oven for 3 h and weighed. The percent yields of the final products were calculated. The dried CC and dried final products (ACC0-600 – ACC3-600) were characterized by FTIR (Spectrum GX, Perkin Elmer, Connecticut, USA), XRD (PW 3040/60, X' Pert Pro Console, Philips, Netherland), FTSEM-EDS (Leo1455VP Electron Microscopy, Cambridge, England), and BET analysis (Micromeritics TriStar II3020, Bavaria, Germany). All products were used as catalysts for the oxidation conversion of nitrite to nitrate in aqueous solution.

## 2.2 Catalytic Oxidation of Nitrite Experiment

The catalytic oxidation of nitrite to nitrate by CC or ACCs follows Eq. (1) [8]:



However, the disproportionation reaction of  $\text{NO}_2^-$  under relatively acidic conditions, which is an undesirable side reaction, may also occur (Eq. (2)) [8]:



Therefore, both catalytic oxidation and disproportionation reaction are considered in this experiment.

## 2.3 The Effect of Dosage

The conversion of nitrite to nitrate by using air as an oxidant under air atmosphere in the absence of light was carried out in batch experiments with ACC2-600 dosage of 0-8 g/L of ACC2-600 in triplicate.

Aqueous 100 mg/L  $\text{NO}_2^-$  solutions (100 mL) containing 0-0.8 g of ACC2-600 were placed into 250 mL conical flasks. The pH of all aqueous solutions was adjusted to 6.5 by using 0.1 M HCl solution (lab grade, Merck, Germany) and NaOH aqueous solutions (lab grade, Merck, Germany) using a pH meter (Mettler Toledo, Hamilton, New Zealand). Subsequently, all solutions were put in a shaking water bath (esstell- ESB, South Korea) and then shaken continuously at 120 rpm at a temperature of  $30 \pm 2^\circ\text{C}$  for 120 min while being open to air atmosphere in the absence of light. After that, the aqueous phase was separated by centrifuge (Onilap-DM0636, USA) at 4000 rpm for 10 min and filtered through a Whatman No. 42 filter paper. The concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  in all filtrates were measured by the diazotization colorimetric method [21]. This is a spectrophotometric method [22], which uses a UV/Visible spectrometer (UNICO 1100, Georgia, USA) detecting  $\text{NO}_2^-$  and  $\text{NO}_3^-$  by measurement of absorbance values at 507 nm, and 220 nm, respectively. The concentrations of the nitrite and nitrate in filtrate solutions were calculated from the absorbance values using a standard calibration curve. The total  $\text{NO}_2^-$  conversion ( $\text{NC}_T$ ) at 120 min was calculated according to (Eq. (3)):

$$\text{NC}_T \% = [(C_{i \text{ nitrite}} - C_{f \text{ nitrite}}) / C_{i \text{ nitrite}}] \times 100 \quad (3)$$

Percent of nitrite conversion via disproportionation reaction ( $\text{NC}_D$ ) from  $\text{NO}_2^-$  lost as NO (Eq. (4)), which was modified from the study of Ying et al. [8]:

$$\text{NC}_D \% = \{[(C_{i \text{ nitrite}} - C_{f \text{ nitrite}}) - (C_{f \text{ nitrate}} - C_{i \text{ nitrate}})] / C_{i \text{ nitrite}}\} \times 100 \quad (4)$$

Where  $C_{i \text{ nitrite}}$  and  $C_{f \text{ nitrite}}$  refer to the initial and final  $\text{NO}_2^-$  concentration, and  $C_{i \text{ nitrate}}$  and  $C_{f \text{ nitrate}}$  refer to the initial and final  $\text{NO}_3^-$  concentration, respectively.

Percent of nitrite conversion via oxidation reaction ( $\text{NC}_O$ ) was calculated following (Eq. (5)) modified form report of Ying et al. [8]:

$$\text{NC}_O \% = \text{NC}_T \% - \text{NC}_D \% \quad (5)$$

## 2.4 The Effect of Reaction Time

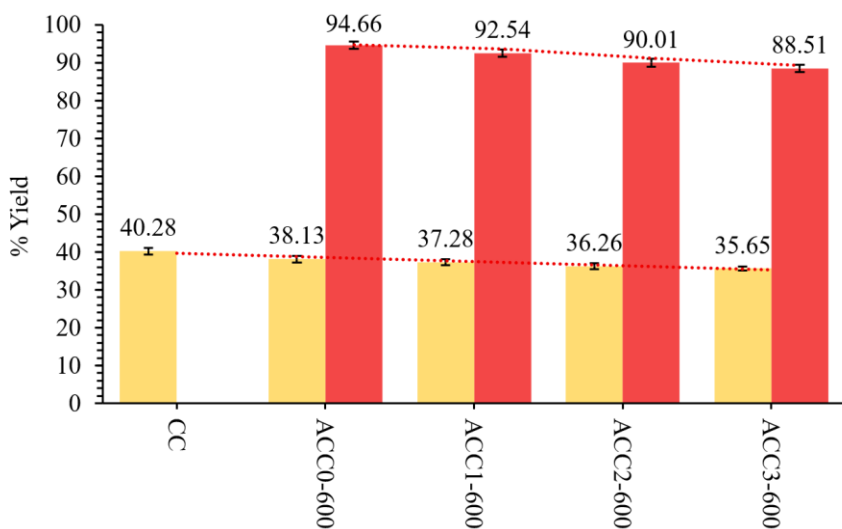
Batch experiments were also used to investigate the effect of reaction time (0-120 minutes) to determine the time needed for maximum conversion. The aqueous solutions (100 mL of 100 mg/L  $\text{NO}_2^-$ ) containing 0 g or 0.3 g (3 g/L) of ACC2-600 were placed into 250 mL conical flasks and put in the water bath to maintain the temperature of  $30 \pm 2$  °C. All experiments were operated in the same way as the experiments used to determine the effect of dosage. Aqueous solution samples were drawn every 15 min and were filtered through a Whatman No. 42 filter paper. The concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  of all filtrates were measured and calculated. The percent of  $\text{NC}_T$  was calculated using Eq (3).

## 2.5 The Effects of NaOH Concentration Activation and Recycling

All experiments were operated in the same way as the time effect experiments with or without 3 g/L of CC or ACC0-600 – ACC3-600 for 60 min. The percentage values of  $\text{NC}_T$ ,  $\text{NC}_D$ , and  $\text{NC}_O$  were calculated using Eqs. (3)-(5). In addition, all remaining catalyst solids obtained after filtration were dried at 50 °C in a vacuum oven (VO500, Memmert, Germany) and weighed (BSA, Sartorius, Germany). All solids were used for catalyst recycling in two subsequent repeats of the reaction. The amount of recovered catalyst used in the repeat reactions was 0.21 g for first recycling round and 0.15 g for second recycling round. Solutions of 100 mg/L  $\text{NO}_2^-$ , 50 mL and 70 mL, were used to maintain a constant dosage concentration of 3g CC or ACCs/L for the first recycling and the second recycling experiments, respectively. All catalyst residues from all reaction repeats were dried and weighed. Percentage of loss values of dried weights of the catalysts in each reaction repeat were calculated and compared. The ACC2-600 residue obtained after all repeat reactions was characterized by FTIR for comparison with fresh ACC2-600.

## 3. RESULTS AND DISCUSSION

### 3.1 Percent Yields of Charcoal and Activated Charcoals



**Fig. 1.** Percent yields of CC and ACCs with 600 W microwave power and 0-3 M NaOH activation, (A) percent yields were calculated based on raw tamarind wood weights and (B) percent yields of ACCs were calculated based on charcoal weights (the error bars represent standard deviation).

Main chemical reactions during NaOH activation have been proposed in the following equations (Eqs. (6) to (10)) [23]:



Minor water-gas reaction with water is also occurring during the microwave activation as described in the following Eq. (11) [14];



Another water-gas shift reaction can take place according to the Eq. (12) [24];



Percent yield of CC made from tamarind wood is quite high (Fig. 1). This is because tamarind wood is hard wood with low volatile matter content (37.82%) and high fixed carbon content (58.30%) [25]. The volatile matters were released by thermal degradation during the carbonization stage. Percent yields of the ACCs obtained after the activation process are low with values in the range between 35.65% and 38.13%, when calculated based on tamarind wood weight, or between 88.51% and 94.66%, when calculated based on CC weight. For 0 M NaOH and 600 W microwave irradiation, the carbon atoms present in the CC performed as good microwave absorbents with induced dipole rotation of carbon-based molecules at the rate of million times per second. This process produced frictional force and released heat for partial oxidation activation [26]. However, the results showed that the percent yield of the partial oxidation (Eqs. (9)-(10)) of some of the original compounds in raw CC and water is a little reduced. In the case of activation with 1 M – 3 M NaOH and 600 W microwave irradiation, the NaOH at various concentrations and some oxygen from air (in the absence of inert gas) resulted in gradual decrease of the ACCs percent yields along with sodium oxide and carbonate species formation, which was attributed to the microwave irradiation. It was shown that the carbon content in CC decreases minimally during activation under these conditions. However, a trend of increasing losses of carbon can be observed with increasing NaOH concentrations. This is attributed to the energized solvated sodium complex, which contains high heat energy, which could cause highly vigorous motions (e.g. translational motion and rotational motion) on the CC surface. This indicates that when higher amounts of NaOH were used more NaOH molecules were available to break the chemical bonds present within the CC matrix, which in turn enhanced the removal of some carbon components in the form of volatiles (e.g. CH<sub>4</sub>, CO<sub>2</sub> or CO) during the process of activation by microwave irradiation [20]. Another role of NaOH is minimizing the formation of tars and any other liquids (dehydrating agents) that could possibly clog up the pores and inhibit the partial oxidation necessary for development of porous structures in the ACCs [26]. This effect allows more NaOH to be exposed to the carbon elements within the CC matrix.

### 3.2 Elemental Composition of CC and ACCs

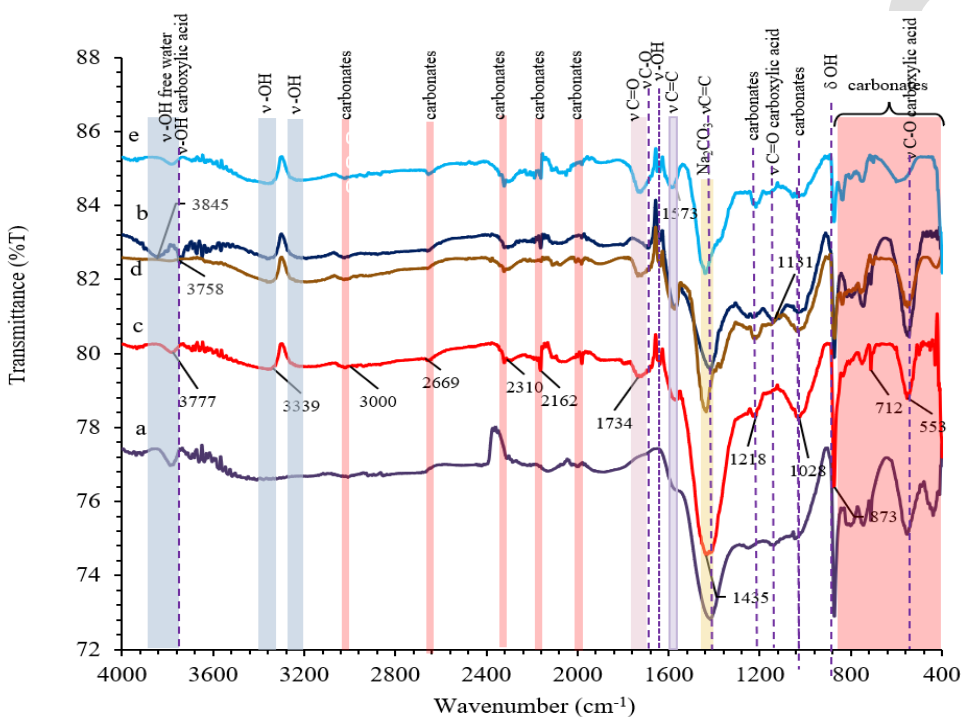
**Table 1.** Elemental composition from EDS of CC and ACCs.

| Samples  | Elements composition (wt.%) |      |     |     |     |
|----------|-----------------------------|------|-----|-----|-----|
|          | C                           | O    | Ca  | Na  | K   |
| CC       | 97.2                        | 2.2  | 0.2 | 0.1 | 0.1 |
| ACC0-600 | 94.1                        | 7.8  | 0.3 | 0.1 | 0.2 |
| ACC1-600 | 90.7                        | 8.0  | 0.3 | 0.8 | 0.3 |
| ACC2-600 | 87.5                        | 9.9  | 0.5 | 1.6 | 0.4 |
| ACC3-600 | 85.7                        | 10.9 | 0.6 | 2.3 | 0.5 |

Table 1 shows that the main element present on the surface of CC and ACCs from tamarind wood is carbon with oxygen acting as the secondary element. In addition, small amounts of Ca, Na, and K elements have also appeared within both CC and ACCs. However, the content of these elements increased after activation with 0 M to 3 M NaOH and 600 W microwave irradiation. The oxygen content has a similar tendency, while the carbon content shows an opposite trend. For CC, the carbon content is quite high. This shows that the carbonization of tamarind wood is quite complete with low oxygen content. Moreover, CC also contains Ca, Na, and K, which are components in the raw tamarind wood. These elements acted as catalysts for the cracking of organic tar compounds [27]. The increasing content of Ca, Na, and K elements, which do not undergo thermal degradation, is attributed to the more extensive degradation of carbon content during activation by 0 M to 3 M NaOH. Especially, Na element content increased with increasing NaOH concentration used for pretreatment and activation. The increasing content of oxygen observed with increasing NaOH concentration from 0 M to 3 M is attributed to the increasing extent of partial oxidation by NaOH in its role as an oxidizing agent and due to the reaction with some oxygen from air during activation. While carbon content was more extensively degraded by thermal gasification by water-gas reaction or water-gas shift reaction (Eqs. (11)-(12)) with increasing

NaOH concentrations, which release CO<sub>2</sub>, CO, and carboxylic acids [20]. These results confirmed that partial oxidation reactions occurred during the activation process.

### 3.3 Surface Chemical of CC and ACCs by FTIR



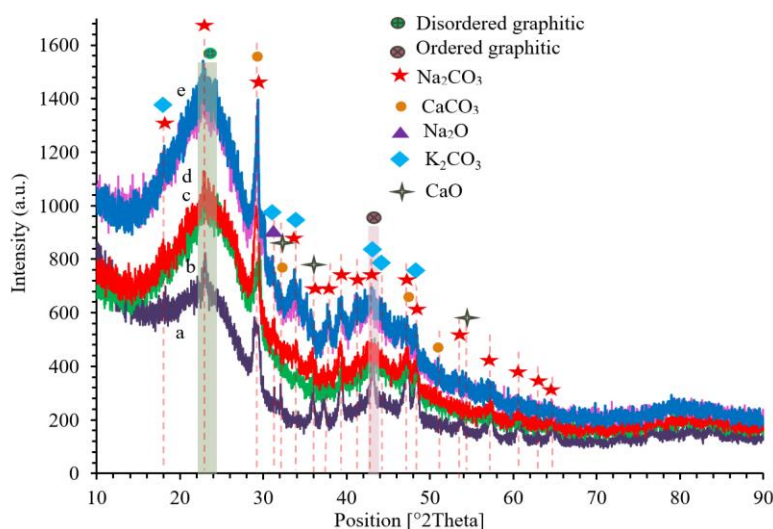
**Fig. 2.** FTIR transmission spectra of (a) CC, (b) ACC0-600, (c) ACC1-600, (d) ACC2-600, and (e) ACC3-600.

FTIR transmission spectrum of CC exhibits smooth spectral lines corresponding to OH, C=C, and C-O functional groups (Fig. 2a). These surface functional groups are attributed to the decomposition of lignocellulosic components via dehydration, carbon rearrangement, and breaking of alkyl-aryl linkages to release water, carbon monoxide, and carbon dioxide molecules during the carbonization process [20]. This has confirmed that tamarind wood is essentially completely carbonized leading to a material with the dominance of aromatic graphitic structure. The OH and CO surface groups formed from adsorbed water

and carboxylic acids, which resulted from the gasification reaction and the reaction of CO with OH<sup>-</sup> ion during carbonization, respectively [23]. While C=C groups represent more extensive development of aromatic carbon character [23]. After activation with only water and 600 W microwave irradiation (Fig. 2b), some functional groups such as OH of the free water of the topmost water layer (free water at 3845 cm<sup>-1</sup>) [28], C=O of the carbonyl [29], and carbonate salts with Na, Ca, and K [30], occurred. These surface functional groups had formed by thermal microwave irradiation and catalytic effects of some compounds present in the original CC. A band between about 3800-3900 cm<sup>-1</sup> can be assigned to the OH group. It corresponds to the stretching mode of free water [28], which penetrated the graphene layers of CC during microwave activation. Furthermore, water-gas reaction, which is based on the reactivity of water vapor in the heterogeneous steam reforming, has also occurred during microwave activation (Eq. (11)) [14] with CO being formed. This CO can also react with OH<sup>-</sup> ion to produce the carboxylic (COOH) acid on close-packed surfaces [24], which is demonstrated through a slight increase of intensities of the peaks at about 3758 cm<sup>-1</sup>, 1131 cm<sup>-1</sup>, and 553 cm<sup>-1</sup>. After activation with NaOH and microwave irradiation, these functional groups decrease or disappear with increasing NaOH concentration. Because carboxylic acid groups were weakened by hydroxyl ions during the NaOH pretreatment stage [20], peaks corresponding to the aromatic structure became dominant with increased intensities of C=C at 1573 cm<sup>-1</sup> and 1435 cm<sup>-1</sup> [23]. This is due to the fact that irradiation with 600 W microwave power could produce enough energy to break the single carbon-carbon bonds inducing the rearrangement reaction of the carbon atoms to form more complex polycyclic structures, while carbon-carbon double bond in the CC cannot be broken with this level of microwave irradiation [20]. Furthermore, the transmission spectra intensities of carbonated groups, especially those dominated by carbonate in the Na<sub>2</sub>CO<sub>3</sub> form, increased with increasing NaOH concentrations from 1 M to 3 M and 600 W microwave irradiation activation (Fig. 2b-e). This result has shown that the more violent activation with NaOH took place and surface carbon structures are formed (Eqs. (6)-(10)). At the same time, OH groups of adsorbed water and penetrated water in graphitic layers of ACCs have remained at a stable level due to strong attraction. On the other hand, the intensity of the C=C group gradually decreased. This showed that the aromatic characteristics of

ACCs decrease a little with increasing NaOH concentrations from 1M to 3M. Finally, the peak corresponding to the C=O group at  $1734\text{ cm}^{-1}$  also underwent a relative increase with increasing NaOH concentration. This peak is attributed to carbonyl groups within the carbon structure, which exist with strong intermolecular interaction between sodium ions and oxygen atoms by a coordinate bond in the carbon structure [29].

### 3.4 Structural Characterization of CC and ACCs by XRD

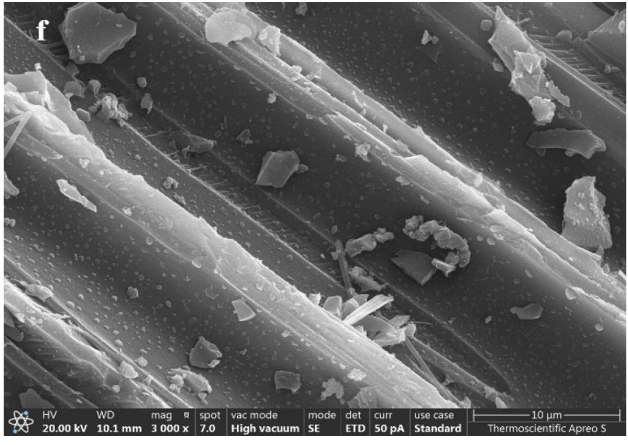
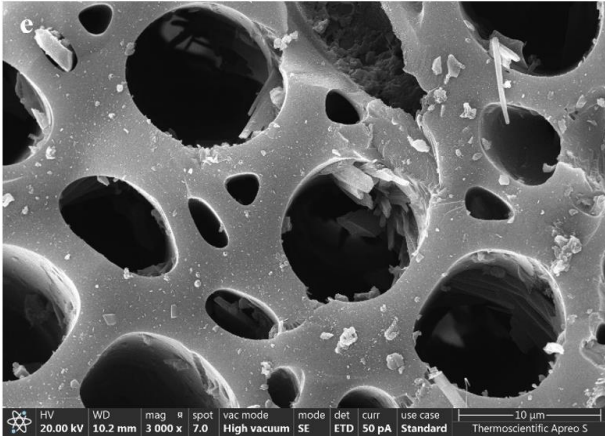
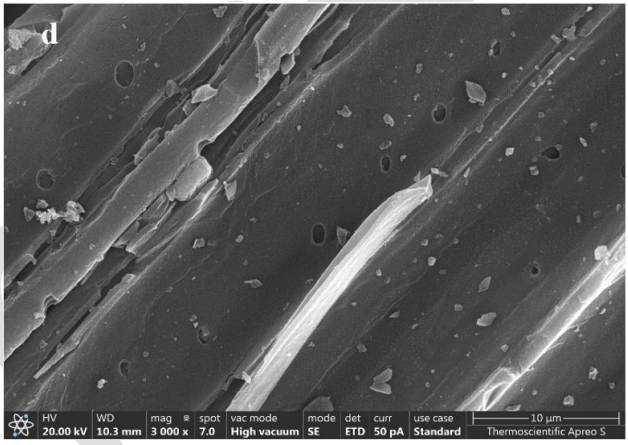
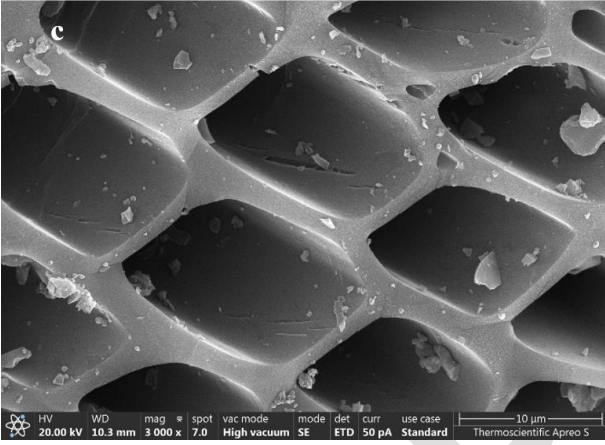
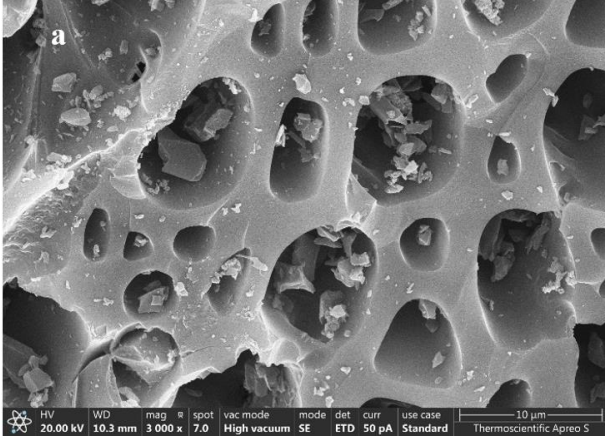


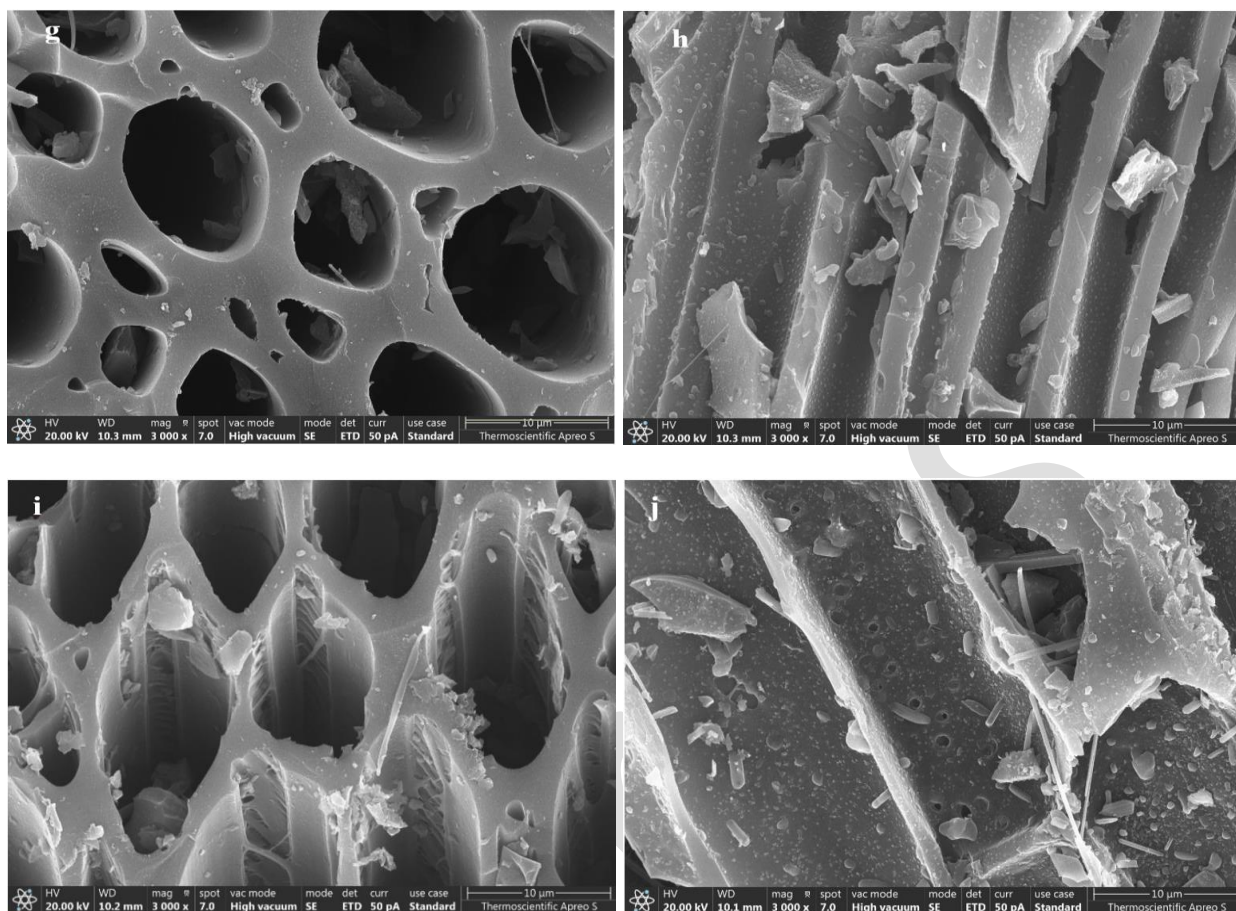
**Fig. 3.** XRD patterns of (a) CC, (b) ACC0-600, (c) ACC1-600, (d) ACC2-600, and (e) ACC3-600.

The XRD patterns of CC and ACCs confirmed the presence of amorphous carbon allotropes and carbonated compounds (Fig. 3a-e), which is consistent with the results of FTIR. All XRD patterns of CC and ACCs exhibit two broad diffractions at  $22.4^{\circ}$  and  $43.5^{\circ}$ , which correspond to the disordered and ordered graphite structures, respectively [31]. However, disordered graphitic characteristics increased with activation by 0 M to 3 M NaOH. This is because alkaline and alkaline earth metal catalysts that remained in ash, or were added with the NaOH, were conducive to inhibiting the graphitization of CC and enhancing the quantity of the amorphous carbon structure in CC and ACCs, which corresponds to the report of Wei et al. [27]. Furthermore, it was seen that the peaks of disordered and ordered graphite

structures, tended to undergo a small shift toward larger angles with increasing NaOH concentration from 0 M to 3 M. This indicated that the stacking thickness of the graphitic layers in ACCs is slightly changing to the thickness of a more amorphous carbon phase [31]. This is attributed to the penetration of H<sub>2</sub>O and metal ions into the graphitic layers causing swelling [18] and the catalytic effect of the metal compounds leading to the cracking of CC and ACCs [27]. At the same time, the compounds K<sub>2</sub>O, CaO, Na<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub> [30, 32-35] are also formed during the carbonization and activation stages by redox reactions (Eqs. (6)-(7)) [23] and carbonate decomposition reaction (Eqs. (8), (10)) [33]. The content of these compounds increases with increasing of NaOH concentrations from 0 M to 3 M. This is attributed to more extensive gasification and partial oxidation of the carbon matrix and increased amount of added Na (Eqs. (9)-(10)) with increasing NaOH concentrations [23].

### **3.5 Surface Morphological Characterization of CC and ACCs by FESEM**



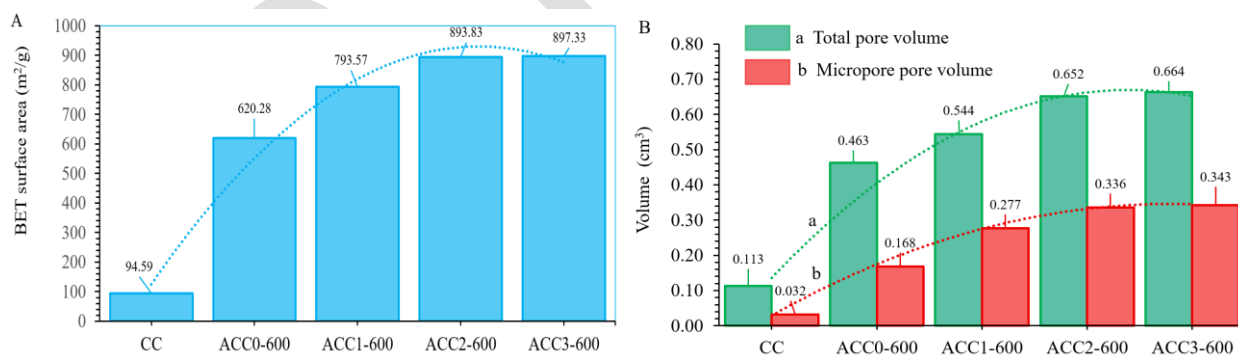


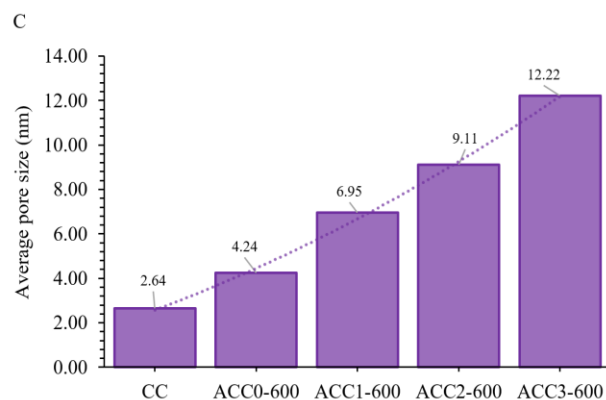
**Fig. 4.** FESEM morphologies of CC (a) cross sectional and (b) longitudinal surface, ACC0-600 (c) cross sectional and (d) longitudinal surface, of ACC1-600 (e) cross sectional and (f) longitudinal surface, ACC2-600 (g) cross sectional and (h) longitudinal surface, and ACC3-600 (i) cross sectional and (j) longitudinal surface.

Surface morphologies of CC showed condensed texture containing a large number of small sized particles adhering on the surface and in the meso-macro hole channel cross section (Fig. 4a). In addition, there are remaining cell walls on the outer surfaces (Fig. 4b). It was shown that the CC structure was only minimally destroyed during the carbonization stage. After activation with 600 W microwave irradiation in the absence of NaOH (only water), morphologies of ACC0-600 showed low number of small adhered particles and a rift on the surface (Fig. 4c-d). Furthermore, the wrinkled cell walls of ACC0-600 have disappeared, while some open holes have appeared. This showed that more carbon degradation took place

through the action of water molecules (from 0 M NaOH) and metal ions (from ash content of raw tamarind wood) during microwave activation. Moreover, the surface morphologies of ACCs have become more fractured and increased with increasing NaOH concentration from 1 M to 3 M for both cross sectional and longitudinal surfaces (Fig. 4e-j). In addition, the number of adhered-small particles also increases with increasing NaOH concentration. This is attributed to the small ionic radius and large dipole moment of the  $\text{Na}^+$  ion, which could be intercalated in-between the layers of charcoal [36], resulting in increased carbon degradation in CC matrix during microwave activation. However, it was seen that the cross-sectional surface texture (hard core) of ACCs is destroyed to a lesser extent than the longitudinal surface texture (soft core), which corresponded to the report of Koshani et al. [37]. This is attributed to the low intensity of microwave for dipole moment of  $\text{Na}^+$  ions that pass through the CC surface. Carbon-based materials have high dielectric loss and low magnetic loss characteristics, which improves the absorption of electromagnetic waves, thereby leading to a reduction in penetration depth with decreasing microwave intensity [38]. However, these morphological characteristics (e.g. meso and macro hole channels and fractures) of ACCs are suitable for adsorption or catalytic heterogeneous reactions [39].

### 3.6 Porosity Characteristics of CC and ACCs





**Fig. 5.** Plots of BET surface area (A), pore volume (B-a) and micropore volume (B-b), and average pore size (C) of CC and ACCs

Surface areas of ACCs are increased by about 5-9 times after activation with 0 M – 3 M NaOH as compared to CC (Fig. 5A). This is attributed to H<sub>2</sub>O, some alkali metals in ash, and NaOH acting as an activating agent by reacting with the carbon material. In addition, microwave heating provides rapid and efficient energy transfer for fast and effective activation. This is consistent with the surface morphological characterization of ACCs from FESEM analysis (Fig. 4). These results have confirmed that the degradation of cell walls and small particles by water and NaOH activation had occurred on the surface of CC with clear open holes and fractures. At the same time, the total pore volumes of ACCs also increased by about 4-6 times from the total pore volume of CC (Fig. 5B-a). Furthermore, the micropore volumes of ACCs are highly increased after activation (Fig. 5B-b). This is the main reason for the significant increases of the surface areas. The average pore diameter values of all ACCs are in range of 4.24 nm to 12.22 nm, which suggested a mesoporous character; however, the significant increase in micropore volume (Fig. 5B-b) indicates the co-development of microporosity. This is attributed to the energized solvated sodium (size 0.93 nm), which undergoes vigorous motions (e.g. translational motion and rotational motion), which could migrate to or insert into the CC surface and create large pores for producing mesoporous ACCs [20]. This result corresponds to the report of Konno et al. [16], which has pointed out that mesopores are formed more extensively after 3 min of 300 W microwave irradiation. Moreover, these parameter values increased with increasing NaOH concentration from 0 M to 3 M.

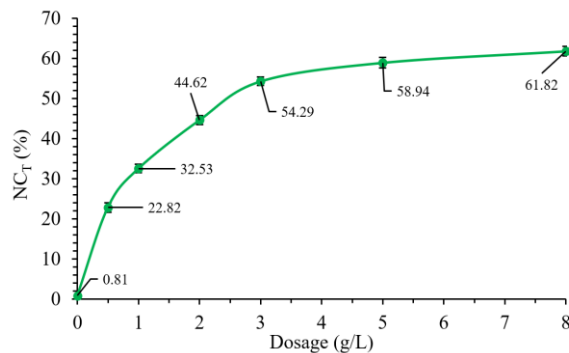
However, the rates of increases in these values declined for increase of the concentration of the NaOH activation from 2 M to 3 M NaOH. This indicated that the increase of the NaOH concentration had facilitated the development of new pores or widened the existing pores present on the surface of the ACCs. However, further increases of the NaOH concentration to 3 M had caused relative increase of porosity parameters. Thus, it can be concluded that the 3 M NaOH concentration was too high and could over-react with the carbon structure and result in the destruction of the pores. Therefore, 2 M is the optimum NaOH concentration for activation of CC to obtain high performing ACCs.

### **3.7 Conversion of Nitrite to Nitrate**

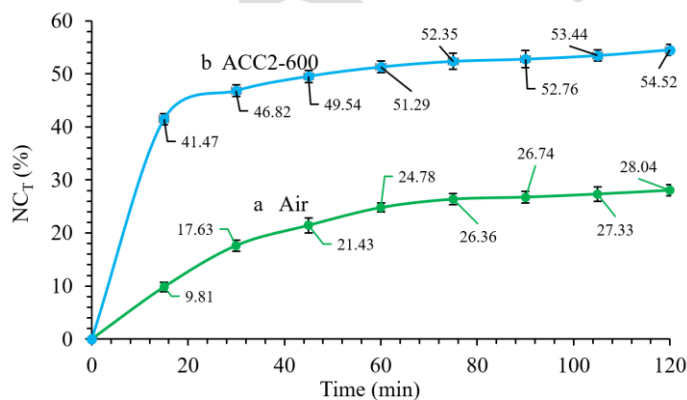
The experiments investigating the conversion of nitrite to nitrate were operated with ambient air in the absence of light at pH 6.5, shaking 120 rpm, and temperature of 30°C. The absence of light eliminates the possibility of microorganism based nitrification activity so that the results are based only on the process facilitated by ACCs catalytic ability [40]. The slightly acidic conditions of pH 6.5 promote main catalytic oxidation (Eq. (1)) and inhibit the formation of the unwanted secondary pollutant NO through the disproportionation reaction (Eq. (2)) [8]. Shaking of the reaction mixture at 120 rpm ensures a constant supply of dissolved oxygen and good contact between the nitrite ions, dissolved oxygen, and the CC or ACCs particles, which improves mass transfer and reaction rates. Finally, the temperature of 30°C provides an optimal thermal environment for the reactions to proceed, preventing excessively high temperatures that could affect the stability of the CC or ACCs and the kinetics of the reaction. For these reasons, these conditions, except the absence of light, are identical with natural conditions of environmental air oxidation reaction [41]. Therefore, the catalytic oxidation reaction by catalysts is almost formed, which is desirable for nitrate formation, because nitrates are more stable, less polluting, and could be used as fertilizer for water plants growth [42].

#### **3.7.1 Effect of dosage and reaction time**

ACC2-600 was collected for the study of the effect of dosage on total nitrite conversion. It was shown that the percent of  $NC_T$  increased with increasing ACC dosage from 0 g/L to 8 g/L (Fig. 6). This is attributed to the increasing surface area available for the adsorption of oxygen and nitrite with increasing dosage. This phenomenon influences the efficiency of the catalytic oxidation. It was confirmed that the nitrite conversion was catalyzed by ACC. It was also seen that the rates of total nitrite conversion increase significantly in the dosage range from 0.5 g/L to 3 g/L and gradually increased with dosage over than 3 g/L. It was shown that further increases of surface for catalytic nitrite oxidation over the dosage of 3 g/L is redundant under these conditions. However, the results achieved with ACC are significantly better than those achieved with zeolite (around 20%-32%) [8] under identical conditions. This may be attributed to the low concentrations of  $H^+$  ion (in form  $H_3O^+$  ion) and dissolved oxygen at pH 6.5 and 120 rpm shaking at 30°C with air atmosphere, even though there is remaining nitrite present. Therefore, the 3 g/L dosage was used in further experiments. Furthermore, an insignificant amount of nitrite conversion occurred in the absence of ACC. It was shown that no disproportionation reaction occurred during the air oxidation process. The effect of reaction time on nitrite conversion was investigated as well (Fig. 7). The results show that nitrite conversion proceeds with high reaction rate within the initial 20 min. The reaction rate for reactions with added ACC declined after 30 min, while it gradually increased for air oxidation in the absence of ACC at all time points. This result is consistent with the report of Ying et al. [8]. It was shown that ACC acted as a catalyst for nitrite oxidation conversion with short reaction time and high percent conversion. The percents of total nitrite conversion in the presence of ACC are higher for the reaction carried out only with air. However, the nitrite conversions in both reactions are continuing with relatively slow reaction rates after 45 min. Therefore, the time point of 60 min was selected for further experiments.

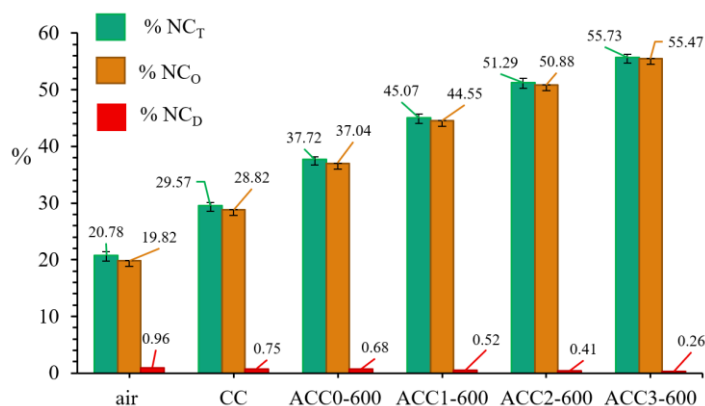


**Fig. 6.** Percent of total nitrite conversion with dosage (0-8 g/L) of ACC2-600 under conditions:  $C_{i \text{ nitrite}} = 100 \text{ mg/L}$ ,  $V=100 \text{ ml}$ , Temperature =  $30 \text{ }^\circ\text{C}$ , Time = 120 min, and  $\text{pH}=6.5$  (the error bars represent standard deviation).



**Fig. 7.** Percent of total nitrite conversion with reaction time (0-120 min) and dosage (3 g/L) of (a) air without ACC, and (b) air with ACC2-600, under conditions:  $C_{i \text{ nitrite}} = 100 \text{ mg/L}$ ,  $V=100 \text{ mL}$ ,  $T=30 \text{ }^\circ\text{C}$ , and  $\text{pH}=6.5$  (the error bars represent standard deviation).

### 3.7.2 Effects of NaOH concentration activation and recycling



**Fig. 8.** Conversion of nitrite to nitrate by only air without catalyst, with CC or ACCs under conditions of  $C_{i \text{ nitrite}} = 100 \text{ mg/L}$ ,  $V = 100 \text{ mL}$ ,  $T = 30 \text{ }^\circ\text{C}$ , Dosage =  $3 \text{ g/L}$  (if used), Time = 60 min, and  $\text{pH} = 6.5$  (the error bars represent standard deviation).

The effects of carrying out the reaction in air without catalyst, in air with CC, and in air with ACC0-600 – ACC3-600 (which are affected by NaOH concentration used for activation), are presented in Fig. 8. It was shown that the values of percents of  $\text{NC}_T$  and  $\text{NC}_O$  are almost identical and increased after the addition of CC or ACCs in comparison to reactions carried out only with air in the absence of CC or ACCs. It was seen that the oxidation reaction of nitrite being converted into nitrate dominates for reaction conditions of  $\text{pH} 6.5$  under air atmosphere in the absence of light with and without catalysts. Furthermore, values of percents of  $\text{NC}_T$  and  $\text{NC}_O$  increased with the addition of ACC0-600, ACC1-600, ACC2-600, and ACC3-600, respectively, while percentages of  $\text{NC}_D$  are very low. This indicates that a near-complete selectivity for the oxidative pathway was achieved with ACCs. It was observed that the percentages of  $\text{NC}_O$  increased dramatically by approximately 8-16 times in comparison with reactions carried out only in air without CC or ACCs, after the addition of CC, ACC1-600, ACC2-600, and ACC3-600, respectively. These results were achieved due to increased surface areas, total pore volume, micropore volume, average

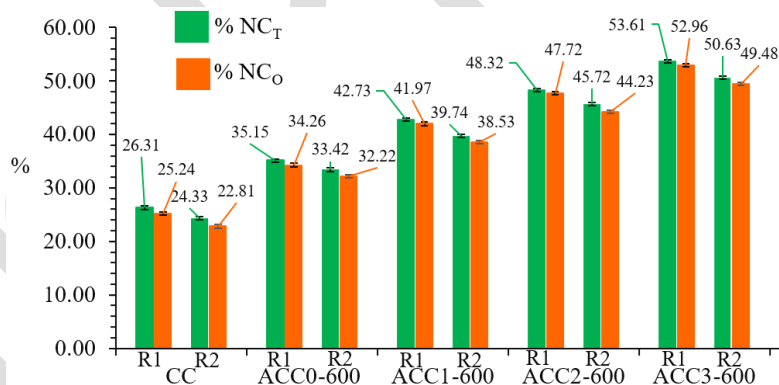
pore size, meso and macro hole channels, surface functional and carbonate observed with increasing NaOH concentration used for ACCs preparations. The reaction mixture can easily enter the meso and macro sized channels [2] for nitrite ion distribution to adsorption on the surface and micropores of CC or ACCs. At the same time, the amount of adsorbed nitrite increased with increasing surface area, pore volume, micropore volume, and micropore size. Micropore volume and micropore size are especially appropriate for nitrite ion adsorption, because the hydrated diameter of nitrite ion is approximately 1.02 nm, which is less than the micropore size of CC and ACCS (2.64-12.22 nm). In addition,  $\text{NO}_3^-$  species were generated from  $-\text{C}=\text{C}$ , and  $-\text{C}=\text{O}$  sites on catalysts surface [7]. This has confirmed that CC or ACCs acted as catalysts for surface catalysis of nitrite oxidation into nitrate with increasing collision probability and promoting the oxidation of  $\text{NO}_2^-$  ion to  $\text{NO}_3^-$  ion [2], while disproportionation reaction was inhibited. However, the products of disproportionation reaction are still formed under all experimental conditions. This is attributed to the small concentration of  $\text{H}^+$  ions that are present in the weakly acidic (pH 6.5) reaction mixture. However, the percents of  $\text{NC}_T$  and  $\text{NC}_O$  achieved with all investigated catalysts are still low in comparison to the report of Ying et al. [8] and Zhang et al. [2], which were carried out using the strongly oxidizing ozone and strongly acidic (pH 3) conditions. However, this approach exhibits mildness and selectivity. This is attributed to the low oxidizing power of oxygen gas and weakly acidic (pH 6.5) condition used in this research. Therefore, the current work must be further developed with the use of d-transition element doping into ACC and biological cooperation for reducing reaction time and further accelerating the catalytic oxidation under flowing water and sunlight. This is expected to improve the performance because microorganisms can efficiently utilize oxygen in solutions with pH values within the range between 6.5 and 8.5 [41]. In addition, it could be applied in hydroponic and aquaponic culture for nitrate use and stimulation toward shifted equilibrium. The effects of air and ACCs catalysts on oxidative nitrite conversion under the conditions used in this research indicated that the oxidation reaction of nitrite by oxygen in air mainly proceeded by adsorption on the surface of CC and ACCs. The adsorption capacity of nitrite ions and oxygen on ACCs increased with increasing NaOH concentration. In addition, the carbonates in CC and ACCs also act as buffers for  $\text{H}^+$  ion adsorption, which reduced the

disproportionation reactions [43] and aided the adsorption of the negative nitrite ions resulting in high catalytic oxidation conversion. At the same time, the buffering action of carbonates also results in the loss of Ca, K, and Na [6]. Moreover, pH 6.5 of the solution is lower than the point of zero charge of these carbonates ( $>7$ ) [44]. Therefore, surfaces of these carbonates consumed protons and attracted  $\text{NO}_2^-$  ions, which can accelerate the oxidation conversion [6]. Furthermore, surface hydroxyl (OH) species and surface carboxyl groups (COOH) could also improve the conversion rate and oxidation of the adsorbed  $\text{NO}_2^-$  ion on the ACCs and into  $\text{NO}_3^-$  ion, and reduce the selectivity of the disproportionation reaction. This is because the oxygen of hydroxide produces hydroxyl radicals from the breakdown of oxygen molecules [2]. Moreover, the negative nitrite ions in solution were drawn closer to the surface of the ACCs by  $\text{Na}^+$  ions within the layers of the ACCs. Therefore, the conversion of nitrite ions during the catalytic oxidation on the surface of the ACCs increased with increasing NaOH concentration used for ACCs activation. This is due to the increased content of the oxygenated functional groups (such as  $-\text{C}-\text{O}$  and OH species) as basic adsorption sites [7]. The disproportionation reaction, which releases NO to gas phase causing secondary pollution [8], has occurred to a very limited extent due to the very low concentration of free  $\text{H}^+$  ions in solution. These results could be summarized in three steps. The first step: nitrite ions from the solution were adsorbed onto the surface of the ACCs. The second step is the catalytic step with ACCs involving a transfer of electrons from the adsorbed nitrite ions to the dissolved oxygen and subsequent nitrate formation. Finally, the nitrate ions are desorbed from the ACCs surface back into the solution.

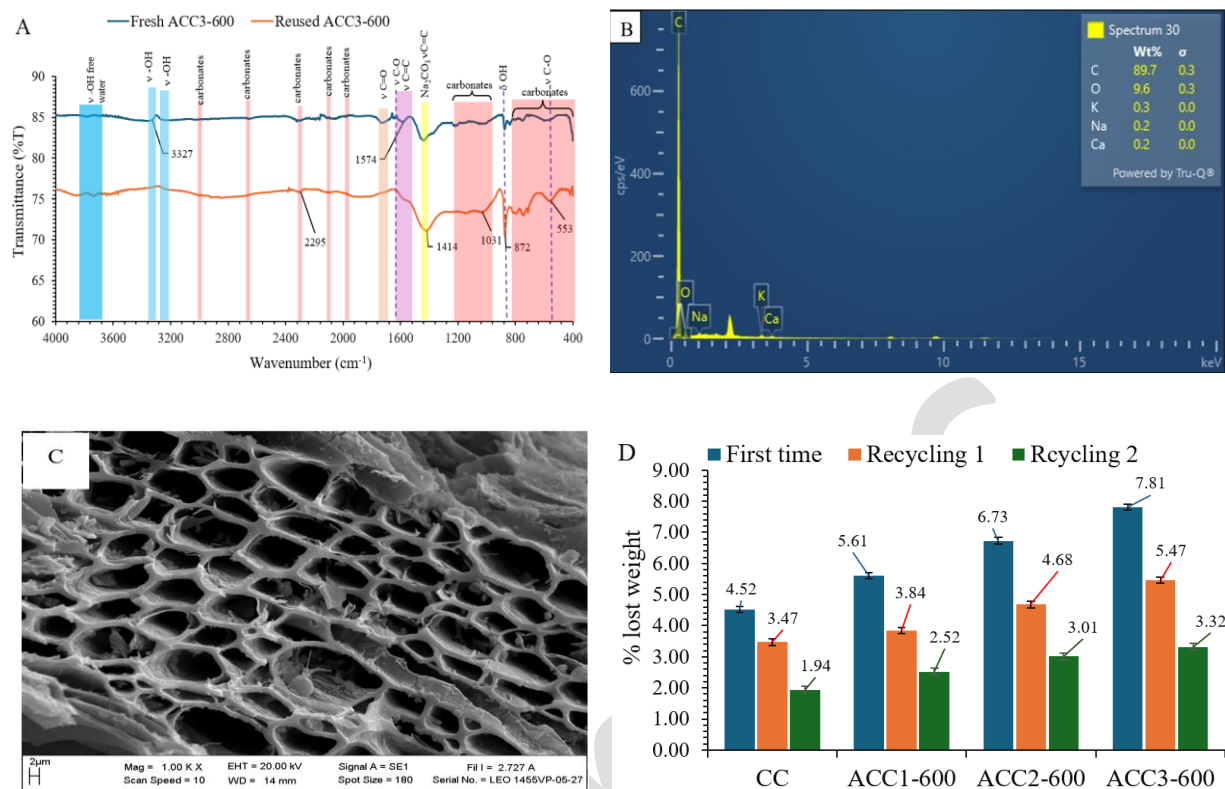
### ***3.7.3 The reusability of the catalyst***

The reusability of the spent catalyst is a key factor to be considered for practical applications [45]. The conversion recycling experiments with CC or ACCs were carried for up to two recycling repeats of the oxidation of nitrite to nitrate to assess the stability of the catalysts. It was found that a relative decrease in the percentages of  $\text{NC}_T$  and  $\text{NC}_O$  for catalyst used in the first and second recycling runs (Fig. 9) was observed across all catalysts in comparison with the fresh catalyst (Fig. 8). Furthermore, differences in the

percentage of  $NC_T$  and  $NC_O$  of spent catalysts increased with increasing number of recycling steps. This may be due to the erosion and leaching of the catalyst particles over many repeats of the operation. However, the conversion performance tends to be similar to effects of NaOH concentration during activation. This may be related to the erosion of carbonates and leaching of small particles during the shaking of the reactions and filtration, which is consistent with hydrodynamic action of carbonate rocks [46] and catalytic oxidation of reactive dye blue 222 by Fe-corn cobs activated carbon catalyst [45]. This is because carbonates are soluble in acidic solutions, and small particles have weak adhesion to solid surfaces [46]. This results in a decrease in the buffering capacity and surface area of the catalysts. Therefore, it may be suggested to increase the reaction time during later recycling or catalyst regenerating experiments. However, it was found that ACCs catalyst demonstrated stable catalytic oxidation activity across three cycles with oxidation conversion efficiency consistently in the range 32.22%-49.48%, which had decreased by 4.82%-5.99%, while disproportionation reaction was effectively suppressed accounting for only 1.15%-1.49% of the conversion.



**Fig. 9.** Percent  $NC_T$  and  $NC_O$  from (a) conversion during first recycling step (R1), and (b) conversion during second recycling step (R2) of nitrite oxidation to nitrate by CC or ACCs under conditions of  $C_{i\text{ nitrite}} = 100$  mg/L,  $V = 70$  mL for first recycling or 50 mL for second recycling,  $T = 30$  °C, Dosage = 3g/L, Time = 60 min, and pH=6.5 (the error bars represent standard deviation).



**Fig. 10.** (A) FTIR transmission spectra of fresh ACC3-600 and reused ACC3-600 after recycling two times, (B) EDS of reused ACC3-600 after recycling two times, (C) SEM of reused ACC3-600 after recycling two times, (D) percent weight loss of CC and ACCs after oxidation conversion at first time, first recycling, and second recycling (the error bars represent standard deviation).

The cycling stability and structural durability of catalysts are critical metrics for evaluating their industrial applicability, as these properties directly determine process economics and environmental benefits [2].

After two steps of recycling, the contents of some carbonate compounds and C=O are reduced, which is confirmed by the FTIR result (Fig. 10-A), as compared to the original catalyst (only ACC3-600 is shown).

This is because carbonates are soluble in acidic solutions [46], while C=O was bonded with hydrogen and transferred to the hydroxyl group of the COOH intermediate, forming water and causing CO<sub>2</sub> to desorb as a molecule [47]. This result has dominated the characteristics of the activated carbon, which exhibits increased intensities of C=C and C-O surface functional groups [48]. Moreover, the bands of nitrite (1260 to 1300 cm<sup>-1</sup>) and nitrate (1330 to 1400 cm<sup>-1</sup>) [49] had not appeared for spent ACC3-600. This indicated

that almost all nitrites had been converted into highly soluble free nitrate ions, and then the soluble free nitrate ions and the remaining very mobile nitrite ions were readily leached into the filtrate during filtration [50]. In addition, EDS investigation of spent ACC3-600 after two recycling steps (Fig. 10-B) showed that the contents of O, K, Na and Ca elements decreased in comparison to the original ACC3-600 (Table 1), while the content of C element increased. This observation was confirmed by the SEM image (Fig. 10-C), which showed some surface erosion and decreased content of small particles in comparison with fresh ACC3-600 (Fig. 4-i). These effects result in decreases of the weights of spent CC and spent ACCs with increasing number of recycling steps (Fig. 10-D). Furthermore, percents of weight loss increased in the order CC, ACC1-600, ACC2-600, and ACC3-600, respectively for all recycling experiments, which is in line with the effects of NaOH concentration during activation. It was shown that carbonate compounds and small particles in the catalysts were eroded during the conversion reactions and filtering. Since the degree of activation increases with increasing NaOH concentration, more carbonates and smaller particles are formed, resulting in a higher percentage weight loss in spent catalysts, which is consistent with the report of Ao et al. [51]. Nevertheless, some carbonates and small particles remained on the spent catalyst because the reaction occurred under weakly acidic conditions and with gentle shaking. Besides, lowering percents of weight loss were observed for all catalysts with increasing conversion recycling time. This is because a large number of carbonates and small particles have been eroded and leached in the first steps of the conversions [52].

#### 4. CONCLUSIONS

The preparations of ACCs were investigated by exploring the effects of NaOH concentration with ratios of CC weight to NaOH weight of 1 g : 0 g, 1 g : 0.04 g, 1 g : 0.08 g, and 1 g : 0.12 g (pretreatment by boiled 0-3 M NaOH solution) and 600 W microwave irradiation activation. It was seen that the percent yields of ACCs gradually decreased with increasing NaOH concentration from 0 M to 3 M, which have values in the range between 35.65% and 38.13 % based on tamarind wood weight calculation or 88.51 and 94.66 % based on CC weight calculation. The elemental composition of CC and ACCs includes

carbon, oxygen, and small amounts of Ca, Na, and K. In addition, it was found that the main carbonate surface functional group of ACCs are present after partial oxidation. At the same time, the contents of amorphous carbon allotropes of ACCs are increased with increasing NaOH concentrations. The swelling of graphitic layers swelling has taken place during the pretreatment by boiling in NaOH solution. The Na<sup>+</sup> ions and water molecules could be inserted into the graphitic layers and rapidly induce surface cracking of ACCs by 600 W microwave irradiation. The extent of surface cracking of ACCs increased with increasing NaOH concentration from 1 M to 3 M for both cross sectional and longitudinal surfaces. These phenomena have resulted in an increase in the porosity of ACCs with average mesopore size in the range from 4.24 nm to 12.22 nm. Furthermore, meso and macro sized hole channels were also presented within the ACCs. These characteristics are suitable for adsorption or catalytic heterogeneous reactions. However, the optimum concentration for the activation of CC to obtain high performance ACCs is 2 M NaOH or 1 g CC: 0.08 g NaOH. Subsequently, the conversions of nitrite into nitrate were affected by CC or ACCs catalysts under air atmosphere in the absence of light, 30 °C, pH 6.5, and 120 rpm shaking. It was found that the nitrite conversions are rapid within 20 min of ACC addition, while they gradually increased in speed for air oxidation without ACC in all times. It was shown that ACC acted as a catalyst for nitrite oxidation conversion with short reaction time and high percent conversion. Moreover, values of percents of NC<sub>T</sub> and NC<sub>O</sub> increased with adding ACC0-600, ACC1-600, ACC2-600, and ACC3-600, respectively, achieving conversion 8-16 times higher in comparison to operations carried out without CC or ACCs, while NC<sub>D</sub> was inhibited. It was shown that ACC significantly enhances the oxidation rate. The high extent of nitrite conversions by catalytic oxidation was ascribed to the high content of surface areas, total pore volume, micropore volume, average pore size, meso and macro hole channels, and carbonate on ACCs products, which could be adapted for natural environment wastewater treatments with decreased operational costs. In addition, spent ACCs can be used for oxidation conversion recycling with 4.82%-5.99% NC<sub>O</sub> efficiency reduction after three recycling steps. However, it was seen that nitrite ions in filtered solutions remain present under these conditions. Therefore, this operation must be further

developed by improving ACC with d-transition element doping and/or biological cooperation for reducing reaction time and increasing the acceleration of catalytic oxidation under flowing water and sunlight.

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### Declaration of generative AI and AI-assisted technologies:

The data and writing process does not pertain to the use of AI tools for data analysis or drawing insights as part of the research itself.

**Author Contributions:** Sumrit Mopoung; Conceptualization, methodology, validation, resources, writing—original draft preparation, supervision, project administration, funding acquisition and writing—review and editing, Rinlaphat Thanakulwaranon; formal analysis, investigation, data curation, visualization; writing—review and editing, all authors have read and agreed to the published version of the manuscript.

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