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Research Article

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Use of a humidity adsorbent derived from cockleshell waste in Thai fried fish crackers (Keropok)

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Abstract: In this research, cockleshell waste from food processing is developed into a humidity adsorbent using a simple technique. Cockleshells were first heated at 1,000°C. The crystal structure, functional group, and morphology of cockleshells before and after heat treatment were investigated. Cockleshells before heat treatment had the aragonite phase of $CaCO_3$ compound, but it transformed into the CaO phase after heat treatment. Next, fried fish crackers, Keropok, were selected for humidity testing. The behavior of the humidity adsorbent and fried fish crackers was investigated for 0–180 days. After humidity testing, the CaO phase of the humidity adsorbent reacted with the humidity or water molecules and transformed into the $Ca(OH)_2$ phase. The amount of crack and roughness on the humidity adsorbent surface increased with the increase in humidity testing time. The humidity adsorbent underwent a high humidity reaction and transformed into $Ca(OH)_2$ after 30 days. The water activity, crispness, and thiobarbituric acid-reactive substances (TBARS) of fried fish crackers were analyzed. The water activity of fried fish crackers rapidly decreased, whereas the crispness slowly decreased in the range of 0–30 days. The humidity adsorbent controlled the TBARS value by increasing slowly. Based on these results, cockleshell waste can be developed as a humidity adsorbent and used to prolong the shelf-life of local food products to at least 90 days.

Keywords: cockleshell waste, calcium hydroxide, humidity adsorbent, heat treatment, fried fish crackers

1 Introduction

Sea animals are of various types such as fish, shrimp, jellyfish, squid, crab, shell, etc. Some of the sea animals can be cooked to a variety of seafoods that have a unique taste and high protein content [1]. Moreover, seafood is popular among people of many religions and nationalities. Thailand is one of the countries that export various types of frozen seafoods due to the Southern Thailand border on the Gulf of Thailand and the Andaman Sea. Pattani province is a small area in Southern Thailand. Most of the Pattani people living near the coastal area are mostly local fishermen involved in fishing, floating basket farming, and seafood processing. Especially, the well-known local fishery is a traditional net fishing technique that using the net with floats and weights [2]. Fisheries provide fresh sea animals as raw materials for seafood restaurants and fresh seafood markets. Nevertheless, the large number of Thai seafood restaurants and food processing by the local people give rise to a considerable amount of seafood waste. For instance, the fresh shrimp provided the waste about a quarter of shrimp [3,4]. The waste management from this seafood waste is a big problem for local officers as a Municipality. Seafood waste not only causes a problem of waste management but also pollutes the air and can disturb the

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coastal tourism in these areas [5]. Though the solution to this waste management is also landfill, the key factor is its unsustainability. So, recycling the waste is a worthy way for zero waste management that follows the United Nation (UN) statements on March 30, 2023 [6]. In addition, this way also results in sustainable waste management for the community and follows the Sustainable Development Goals (SDGs) of Thailand policy [7]. Thus, the cockleshell waste from Thai seafood processing, approximately 579 tons per year in Pattani, is considered for the study [8,9]. Cockleshells, widely used as a source for animal feed, soil additive, and additive to structural and paper industries, consist of more than 95% of calcium compound [10]. However, these calcium compounds are utilized due to the complex recycling process and cannot operate with the local people [11].

Therefore, this work focuses on developing calcium sources from cockleshell waste with a simple technique that can be used in the Pattani community following the SDGs. Nonetheless, our previous works present the success of the development of humidity adsorption material from various calcium sources [12–14]. So, the aim of this work is to develop the cockleshell waste in Pattani as a humidity adsorbent that the local people can use.

Additionally, fried fish crackers, namely Keropok, a famous local snack and an appetizer in pub and bar restaurants, were used in the study [15]. Production of fried fish crackers is encouraged by the Thai government policy as a "One Tambon (sub-district) One Product; OTOP," causing the fried fish crackers to be recognized and made available in tourist towns and all regions of Thailand [16]. Fried fish crackers were contributed by hawkers from Pattani. As the fried fish crackers were produced without food additives and preservatives by households or small enterprises in the Pattani community, the crispness of this fried fish crackers may be easily decreased by the humidity during the delivery and marketing [17].

Consequently, the humidity adsorbent of this work was developed from cockleshell waste by the heat treatment process. The cockleshells before and after heat treatment were characterized for their crystal structure, functional group, and morphology. Afterward, the humidity adsorbent was applied with fried fish crackers and characterized. The humidity adsorbent before and after humidity testing was analyzed for the crystal structure, functional group, and morphology. However, the water activity, crispness, and thiobarbituric acid-reactive substances (TBARS) of fried fish crackers before and after humidity testing were addressed.

2 Materials and methods

2.1 Preparation of the humidity adsorbent and fried fish cracker

2.1.1 Humidity adsorbent preparation

Cockleshells were collected from a local seafood restaurant at Rusamilae subdistrict in Pattani province, Thailand. The cockleshells were soaked in fresh water for 24 h. Then, they were cleaned and polished to remove the soil and organic matter contamination. The cockleshells were air-dried for 12 h under atmospheric pressure at room temperature. The cockleshells were crushed by a jaw crusher machine (Retsch, model BB200) and ground by a grinder machine (SPEX CertiPrep, model 8000-D Mixer Mill) to get cockleshell powder. The cockleshell powder was passed through a sieve of stainless steel (Endecotts, pore size: 106 μm) as the particle size was less than 100 μm. Next, the cockleshell powder was heated up to 1,000°C using a high-temperature furnace (Carbolite, AAF1100/18) with a heating rate of $5°C\cdot min^{-1}$ for 4 h and cooled down in a furnace to room temperature. Then, 3 g of cockleshell powder was filled in a tea filter bag and heat-sealed as a humidity adsorbent. Eight groups of humidity adsorbents were made for humidity adsorption testing for 0, 5, 10, 20, 30, 60, 90, and 180 days and stored in a desiccator to prevent exposure to humidity.

2.1.2 Fried fish cracker preparation

Sheet-dried fish crackers (fresh fish crackers) were purchased from the people of Thailand Muslim community in Pattani, Thailand. Samples with an approximate diameter of 40 mm, a thickness of 2 mm, and a weight of 1.25 g were selected from the sheet-dried fish crackers. Then, all samples were fried at 180°C using an electric deep fryer containing 2 l of palm oil. The samples were put in the frying stainless steel basket ($18 \times 20 \times 11\ cm^3$) and then dipped into palm oil for 30 s. Then, the fried fish crackers were drained on a screen for 5 min and blotted with a paper towel to remove the excess oil. All fried fish crackers were allowed to cool at room temperature for 15 min. Finally, 15 g of fried fish crackers was taken in a polyethylene terephthalate plastic bag with a size of $175 \times 210\ mm^2$ for humidity adsorption testing under various conditions and stored in a desiccator to prevent humidity exposure.

2.2 Humidity adsorption testing and characterization

2.2.1 Humidity adsorption testing

For humidity adsorption testing, a humidity adsorbent and a fried fish cracker were taken and heat sealed and tested for various time ranges. After humidity adsorption testing was carried out, the behavior of fried fish crackers without a humidity adsorbent (control) and with 3 g of humidity adsorbent was investigated at 0, 5, 10, 20, 30, 60, 90, and 180 days.

2.2.2 Characterization of cockleshell powder before and after humidity adsorption testing

For characterization of the cockleshell powder before humidity adsorption testing, its crystal structure and phase transformation before and after heating at 1,000°C were investigated by X-ray diffraction (XRD, Rigaku SmartLab SE). The XRD was performed with CuKα radiation (λ = 1.54 Å) at 30 kV and 40 mA in a 2θ range of 10°–80° with a scan step of 0.02°. The XRD patterns were used to obtain the quantitative phase composition by Rietveld refinement using the Match! Program, version 4.0. The functional groups of cockleshell powder before and after heating at 1,000°C were analyzed by Fourier transform infrared (FTIR) spectroscopy (PerkinElmer, Spectrum Two) in a range of 4,000–400 cm^{-1} with a resolution of 1 cm^{-1}. The morphology of cockleshell powder before and after heating at 1,000°C was monitored by scanning electron microscopy (SEM, Thermo Scientific, Axia ChemiSEM). The samples were put on carbon tape and coated with gold using sputtering for 30 s. The SEM image was converted to the grayscale. The rectangular zone of the SEM image was selected and analyzed for the surface roughness (R_a) by the ImageJ program, version 1.54d. After humidity testing of the humidity adsorbent, the XRD, FTIR, and SEM techniques were also used to identify the phase transformation, functional groups, and morphology.

2.2.3 Characterization of fried fish crackers before and after humidity adsorption testing

The water activity of fried fish crackers before and after humidity adsorption testing was determined using a water activity meter (AquaLab 4TE). The fried fish crackers were ground by an agate mortar and pestle. About 2 g of fried fish cracker powder was placed in a water activity tray [18,19]. For the penetration test before and after humidity adsorption testing, the crispness of fried fish crackers was measured using a Texture Analyzer (Stable Micro Systems, TA.XTplus). The fried fish crackers were placed onto a heavy-duty platform/crisp fracture support rig and a spherical probe (P/0.25) was used. The conditions of the Texture Analyzer were a test speed of 2.0 mm·s^{-1}, a probe travel distance of 5 mm, and a trigger force of 5 g. The penetration test was repeated till precision data were obtained. TBARS in fried fish crackers were determined according to the method recommended by Tarladgis et al. and expressed as mg of malondialdehyde per kg (mg MDA·kg^{-1}) sample [20]. The water activity, crispness, and TBARS of fried fish crackers without a humidity adsorbent (control) and with 3 g of humidity adsorbent were analyzed and addressed.

3 Results and discussion

3.1 Characterization of cockleshells

The cockleshell waste was collected from a local seafood restaurant and ground into cockleshell powder. The cockleshell powder was studied by the FTIR technique for determining functional groups, and the results are shown in Figure 1.

Figure 1 displays the FTIR spectrum of cockleshell powder, which shows peaks at 713 cm^{-1} (ν_4), 858 cm^{-1} (ν_2), 1,468 cm^{-1} (ν_3), and 1,083 cm^{-1} (ν_1), assigned to the C–O symmetric bending vibrations of CO_3^{2-} [21,22]. The peaks at 1,231 cm^{-1} and 1,742 cm^{-1} corresponded to the stretching vibrations of C–O and C═O of CO_3^{2-}, respectively. These

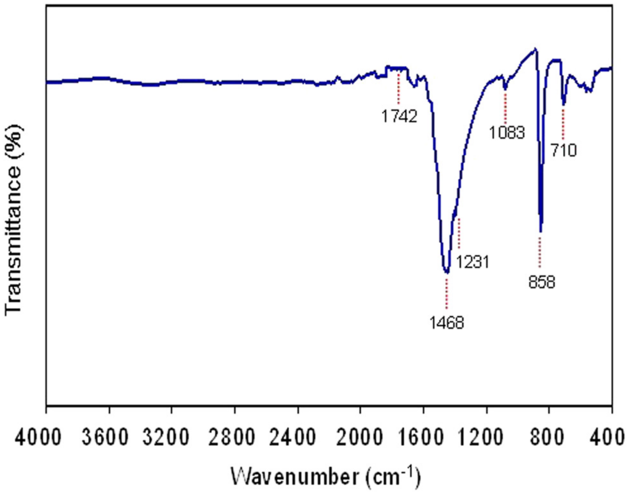

Figure 1: FTIR spectrum of cockleshell powder.

results confirm that the cockleshell powder has a carbonate group.

Next, the crystal structure of cockleshell powder was investigated by the XRD technique, and the XRD pattern is shown in Figure 2.

Figure 2 displays the XRD pattern of cockleshell powder, which shows peaks at 2*θ* ≈ 26.32, 33.24, 37.96, 45.96, and 52.52°, assigned to the aragonite phase of calcium carbonate ($CaCO_3$) compound according to the Joint Committee Powder Diffraction Standard (JCPDS) No. 05-0453. This result is related to the carbonate group and in good agreement with the FTIR result.

Then, the morphology of cockleshell powder was analyzed by the SEM technique, and the SEM image is shown in Figure 3.

Figure 3 shows the morphology of cockleshell powder, which revealed dense accumulated layers of needle and rod shaped sheets, indicating aragonite sheet layers. This morphology is commonly found in shells [23].

After the cockleshell powder was heated at 1,000°C for 4 h, the functional group of cockleshell powder was analyzed by FTIR, and the spectrum is shown in Figure 4.

The FTIR spectrum of cockleshell powder after heating at 1,000°C for 4 h (Figure 4) shows peaks at 870 and 1,068 cm^{-1}, assigned to the symmetric stretching vibration of C–O [24]. The peak at 451 cm^{-1} is assigned to symmetric vibrations of Ca–O [25]. This means that the FTIR spectrum of cockleshell powder after heating did not show a carbonate peak, as compared with cockleshell powder before heating, and this confirms that the heating at 1,000°C can decompose the carbonate group in the cockleshell powder.

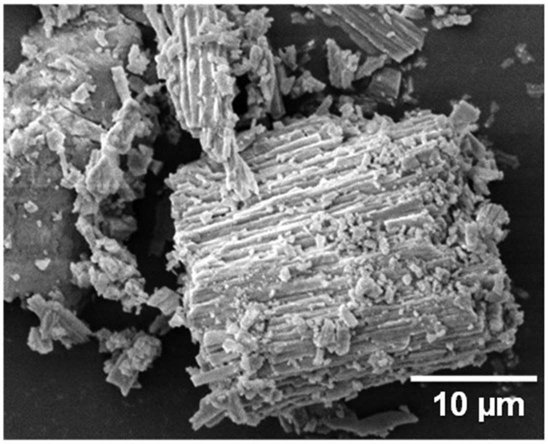

Figure 3: Morphology of cockleshell powder.

The decomposition of calcium carbonate of cockleshell powder was confirmed by investigating the crystal structure and phase transformation by XRD (Figure 5).

Figure 5 displays the XRD pattern of cockleshell powder after heating at 1,000°C for 4 h, which shows peaks of 2*θ* at 32.30, 37.45, 53.95, 64.25, and 67.45°, which is a lime phase of calcium oxide (CaO) according to the JCPDS No. 82-1691. The XRD results indicated that the aragonite phase of cockleshell powder can be completely transformed into calcium oxide. During heat treatment at 1,000°C for 4 h, calcium carbonate consists of carbonate ions (CO_3^{2-}) and calcium ions (Ca^{2+}). The carbonate ion has a covalent bond, whereas the calcium ion has an ionic bond. This is because the covalent bond has a lower bond strength than the ionic bond. So, the carbonate group of calcium carbonate in cockleshell powder was

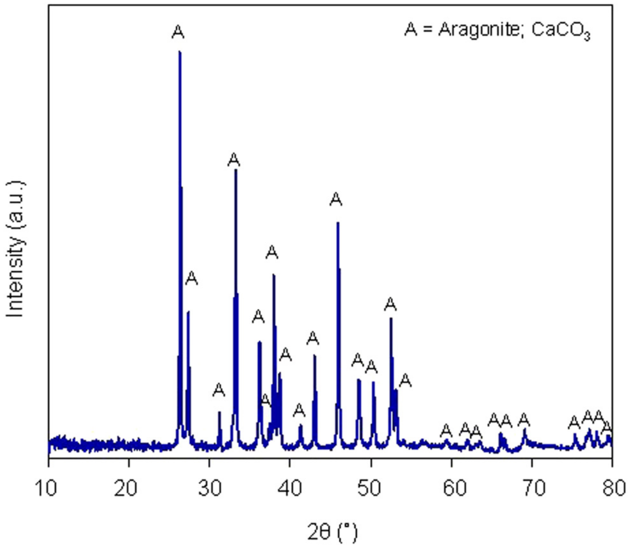

Figure 2: XRD pattern of cockleshell powder.

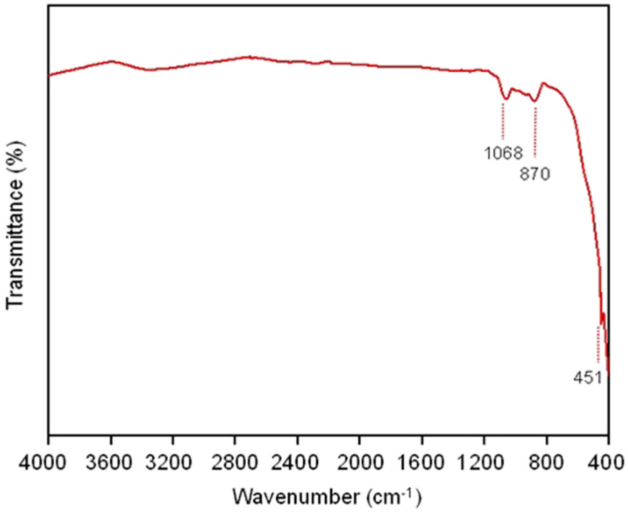

Figure 4: FTIR spectrum of cockleshell powder after heating at 1,000°C for 4 h.

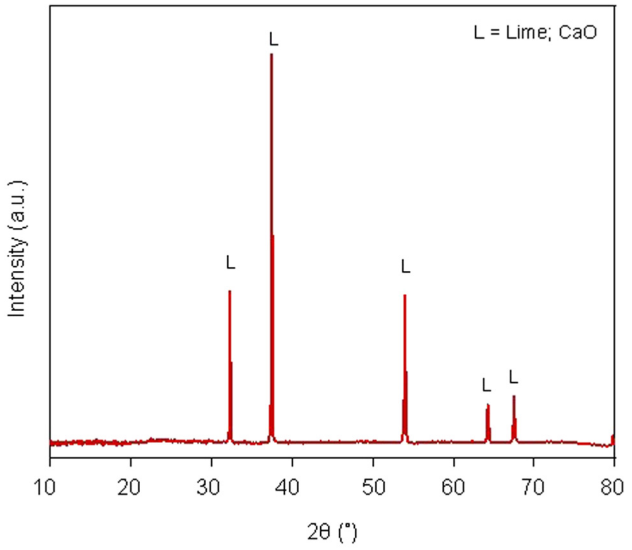

Figure 5: XRD pattern of cockleshell powder after heating at 1,000°C for 4 h.

released at a high temperature of 1,000°C following Eq. 1 [10].

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

Moreover, the morphology of cockleshell powder after heating at 1,000°C for 4 h was analyzed by SEM, and the SEM image is shown in Figure 6.

The morphology of cockleshell powder after heating at 1,000°C for 4 h (Figure 6) shows a fragile cylindrical shape (spherical shape interconnected to a skeleton structure) with a smooth surface. The fragile cylindrical shape had an average diameter of approximately 5 μm. Moreover, the fragile cylindrical shape had an agglomeration and interconnection like a skeleton structure that is commonly found in the calcium oxide compound [12,26]. Normally, calcium oxide has a hydrophilic property and easily interacts with water molecules [27]. So, the fragile cylindrical shape of calcium oxide compound from cockleshell waste is interesting to further study in more detail its potential for humidity adsorption in fried fish crackers.

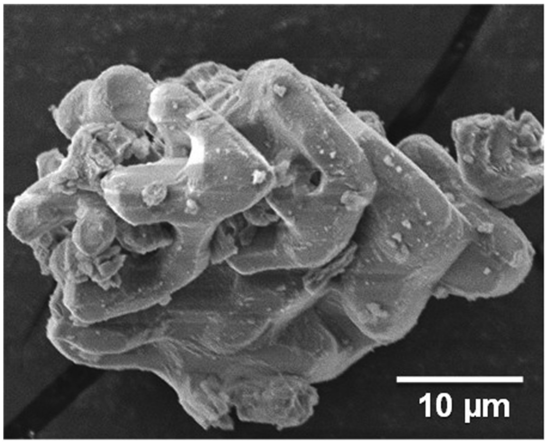

Figure 6: Morphology of cockleshell powder after heating at 1,000°C for 4 h.

3.2 Humidity adsorption testing of cockleshell powder

The humidity adsorbent (heat-treated cockleshell powder) prepared from cockleshell powder was applied with fried fish crackers, and the humidity adsorption was studied on 0, 5, 10, 20, 30, 60, 90, and 180 days. The functional groups of humidity adsorbent after humidity adsorption testing were identified by FTIR, and the results are shown in Figure 7.

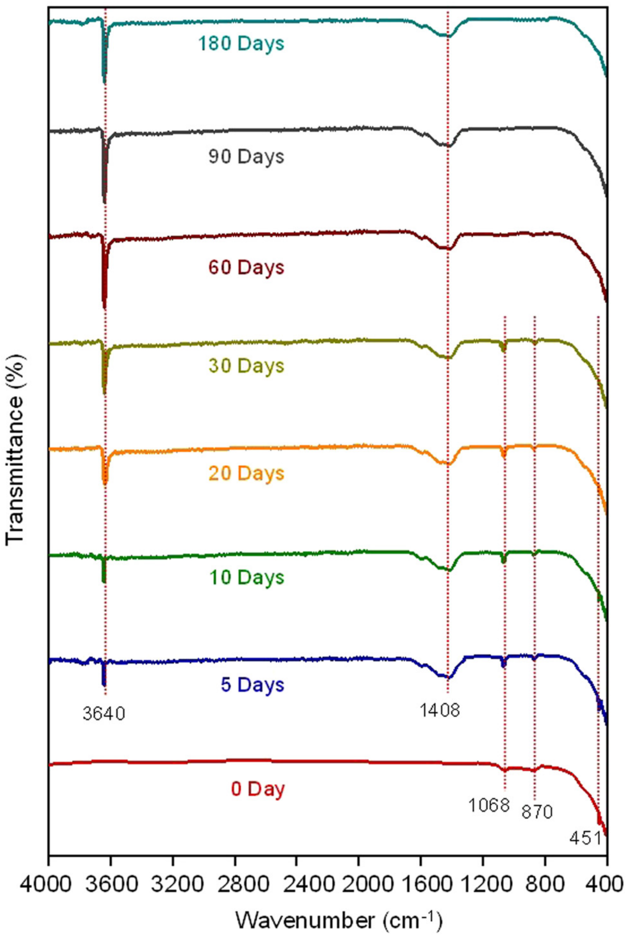

Figure 7: FTIR spectra of the humidity adsorbent from cockleshell powder for the testing time range of 0–180 days.

Figure 7 presents the FTIR spectrum of the humidity adsorbent, which shows a new strong peak at 3,640 cm^{-1} as compared with that before humidity adsorption testing. This intensity of new peak was assigned to the O–H stretching vibration of water molecules after humidity testing from 5 to 180 days [28]. The new peak increased the intensity with increasing humidity adsorption testing time. In addition, the FTIR spectrum of the humidity adsorbent still shows a broadened peak around 1,408 cm^{-1}, assigned to the asymmetric stretch of O–C–O corresponding to CO_3^{2-} ions [29]. These CO_3^{2-} ions were from the $Ca(OH)_2$ compound or hydrated lime phase that resulted due to the carbonation reaction between $Ca(OH)_2$ and CO_2 gas from the atmosphere [30]. The disappearance of CaO peaks at 60 days was attributed to the CaO phase of the humidity adsorbent transforming into the $Ca(OH)_2$ phase due to the reaction of CaO with humidity or water molecules.

Moreover, the crystal structure and phase composition of the humidity adsorbent are shown in Figure 8.

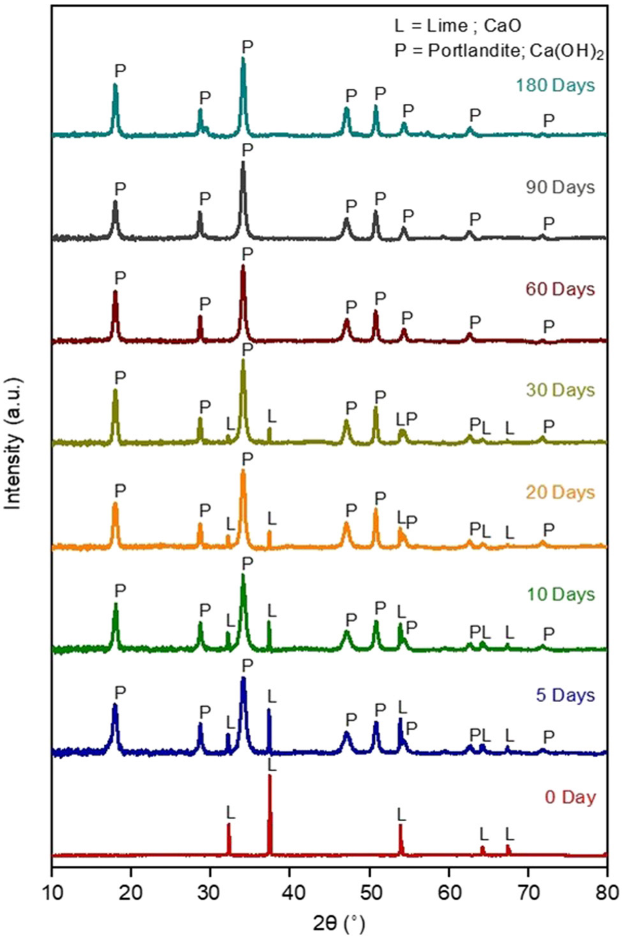

Figure 8: XRD patterns of the humidity adsorbent from cockleshell powder for the testing time range of 0–180 days.

In Figure 8, the XRD patterns of the humidity adsorbent initially at day 0 show only the phase of CaO. The XRD patterns of the humidity adsorbent at day 5 show new peaks at 2θ of 17.95, 28.70, 34.05, 47.10, 50.85, 54.45, 62.75, and 71.90° corresponding to JCPDS No. 44-1481 of the portlandite phase of calcium hydroxide ($Ca(OH)_2$) compound [31]. While the intensity of CaO as an initial phase decreased, the CaO compound adsorbs the humidity or water molecules resulting in the transformation to $Ca(OH)_2$ according to Eq. 2 [32].

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \tag{2}$$

Considering the XRD pattern of $Ca(OH)_2$, the intensity increased with the increase in the humidity adsorption testing time from 10 to 90 days, indicating that the humidity adsorbent adsorbed the humidity or water molecules. However, the XRD pattern of CaO decreased from 0 to 30 days and disappeared at 60 days. The disappearance of CaO indicated that CaO had completely transformed to $Ca(OH)_2$ by reacting with humidity or water molecules. Then, the XRD pattern of only $Ca(OH)_2$ was observed during 60–180 days, and there was no change in the XRD pattern intensity.

Next, the intensity of XRD patterns of the humidity adsorbent was studied in the time range of 0–180 days, and the quantitative phase composition was calculated by Rietveld refinement [33]; the results are shown in Figure 9.

Figure 9 shows that the CaO phase rapidly decreased after 60 days of humidity adsorption testing. At the same time, the $Ca(OH)_2$ phase rapidly increased after 60 days.

To clarify the phase transformation of the humidity adsorbent from CaO to $Ca(OH)_2$, the XRD patterns at 0 and 60 days were confirmed by Rietveld refinement, as shown in Figure 10.

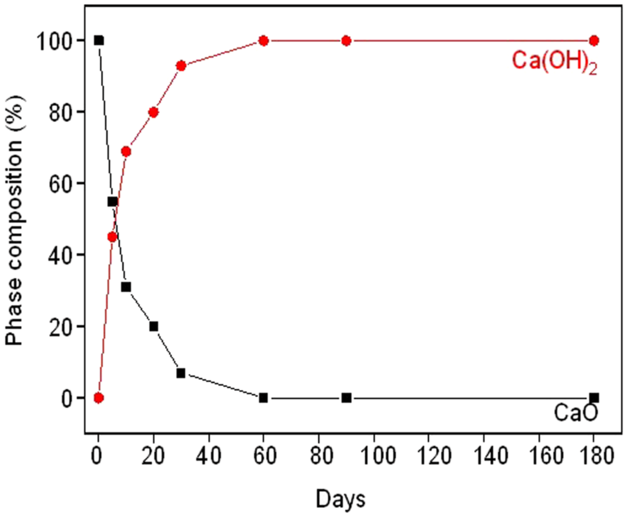

Figure 9: Quantitive phase compositions of cockleshell powder after humidity adsorption testing.

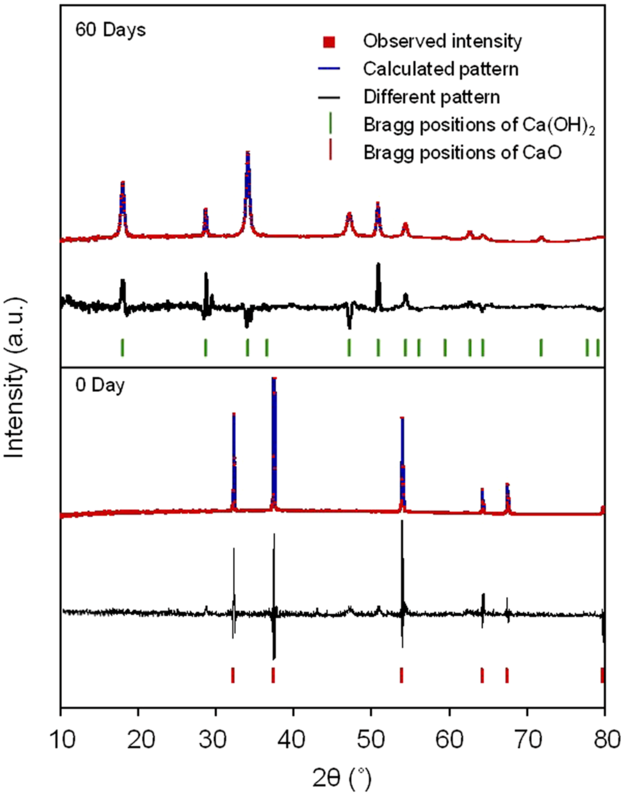

Figure 10: Quantitive phase compositions of the humidity adsorbent after humidity testing at days 0 and 60.

Figure 10 shows that only the lime phase was present at day 0, whereas only the $Ca(OH)_2$ phase was present at 60 days. It means that the CaO phase of the humidity adsorbent can be completely transformed into $Ca(OH)_2$ within 60 days.

The morphology of the humidity adsorbent was identified by SEM, and the SEM images are shown in Figure 11.

Figure 11(a)–(d) shows the morphology of the surface of the humidity adsorbent after humidity testing from 5 to 20 days; it still has a smooth surface similar to that at day 0 (before humidity testing). However, the humidity adsorbent after humidity testing for 30 days showed some of the microcracks on the surface.

After 30 days of humidity testing (Figure 11(e)–(h)), the crack on the surface clearly showed an increase with the increase of humidity testing time. This means that the appearance of the crack on the surface was due to the skeleton structure of CaO that adsorbed the water molecules and then swelled [12,34,35].

In addition, the surface roughness of the humidity adsorbent was analyzed on ten areas of SEM images using the ImageJ program [36]. The topography of each humidity adsorbent is shown at the right corner of Figure 11 images. The relationship between the average surface roughness (R_a) [37] and the humidity testing time is shown in Figure 12.

The average surface roughness of the humidity adsorbent during the humidity testing time of 0–20 days slightly increased with increasing humidity testing time. However, the average surface roughness of the humidity adsorbent between 20 and 30 days increased from 170.90 to 175.38 µm. Moreover, the average surface roughness dramatically increased after 30 days of humidity testing. This means that the increase in average surface roughness value results from the humidity adsorbent that adsorbed the humidity or water molecules. These results can confirm the previous results and explain the swelling of the skeleton structure.

3.3 Characterization of fried fish crackers

To prevent the spoilage from microorganisms and extend the shelf-life of fried fish crackers, an important parameter to control is water activity. The water activity on the surface of fried fish crackers was measured and is shown in Figure 13.

The initial water activity (day 0) of fried fish crackers was on average 0.26 a_w. Generally, the fried fish crackers have the water activity in the range of 0.30–0.40 a_w [38]. This indicates that these fried fish crackers have a low level of water activity. During the test, the fried fish crackers with humidity adsorbent had water activity in the range of 0.26–0.32 a_w, while that of control was in the range of 0.26–0.67 a_w. The water activity value of the control is higher than that of the humidity adsorbent for all humidity testing time. However, fried fish crackers with the humidity adsorbent show a decrease of water activity during the humidity testing time of 0–30 days. This dramatic decrease in water activity resulted from the humidity adsorbent that adsorbed the humidity or water molecules. This means that the humidity adsorbent with a CaO phase has high sensitivity in the reaction of humidity or water molecules. Additionally, the water activity after the humidity testing time of 30 days slightly increased from 0.14 a_w to 0.17, 0.22, and 0.32 a_w at 60, 90, and 180 days, respectively. These results show that the potential of humidity adsorbent is close to the saturation point or like a constant slope of a linear relationship (about 60 days of humidity testing time) and relates to the complete phase transformation of humidity adsorbent from CaO to $Ca(OH)_2$. Although the humidity adsorbent is close to the saturation point, the water activity value of fried fish crackers slightly increased. In addition, the water activity of fried fish crackers with the

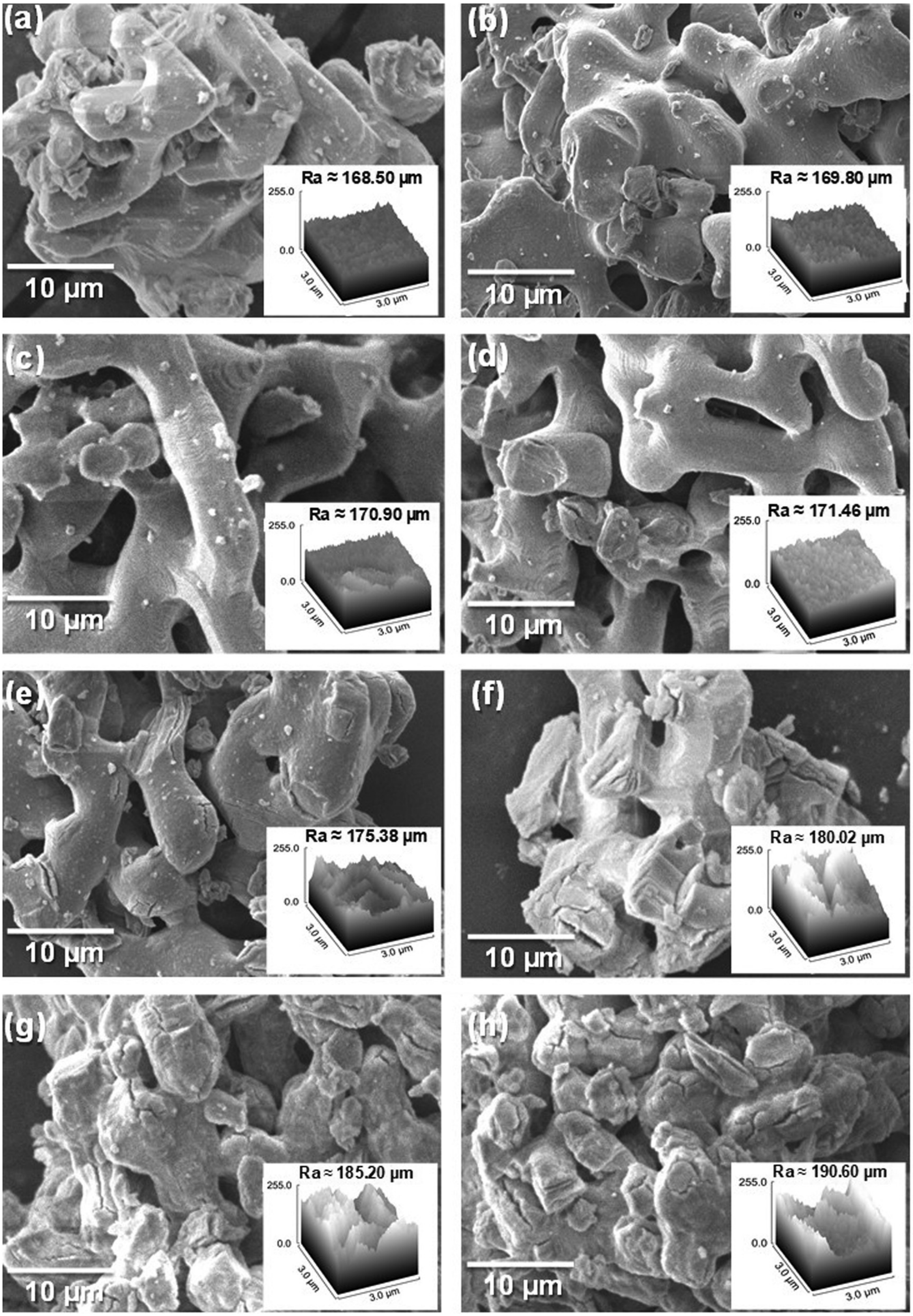

Figure 11: Morphology of the humidity adsorbent after humidity testing at (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 60, (g) 90, and (h) 180 days.

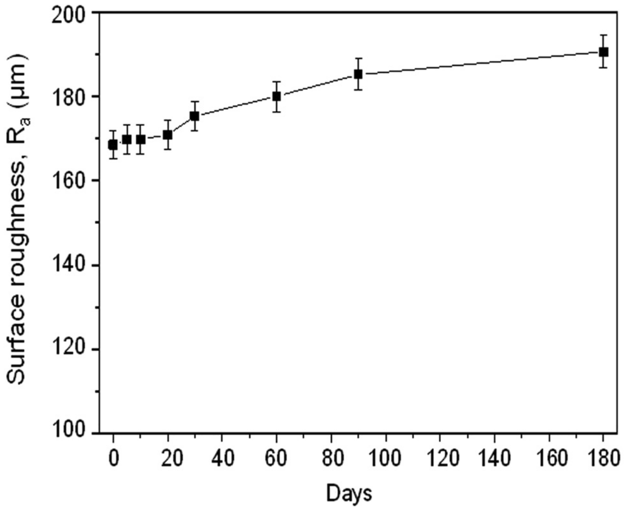

Figure 12: Average surface roughness of the humidity adsorbent after humidity testing in the range of 0–180 days.

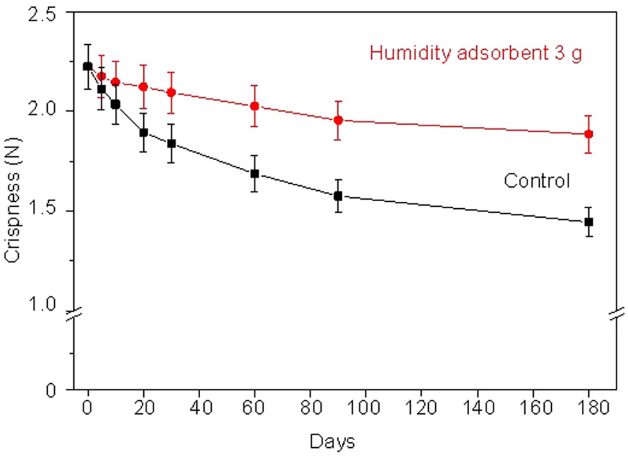

Figure 14: Crispness of fried fish crackers without humidity adsorbent (control) and with 3 g of humidity adsorbent for various humidity testing times.

humidity adsorbent at 180 days was still 0.32 a_w. This water activity can prevent microorganism growth and prolongs the shelf-life of fried fish crackers [38].

Crispness is an important parameter of fried fish crackers for consumer attraction. The crispness results are shown in Figure 14.

From Figure 14, the initial crispness (0 day) of fried fish crackers had the highest value of 2.22 N. The fried fish crackers with humidity adsorbent have a crispness in the range of 2.22–1.88 kg·force, while that of control was 2.22–1.44 N. The crispness value of fried fish crackers with the humidity adsorbent is higher than that of the control during all humidity testing times. The crispness of fried fish crackers with the humidity adsorbent did not significantly decrease after a humidity testing time of 0–30 days when compared with the control. The humidity adsorbent adsorbed the humidity or water molecules that transmit into the air cell structure of fried fish crackers resulting in a fluidizing network. The fluidizing network in the fried fish crackers makes the crispness decrease [39]. After 30–180 days of testing, the crispness of fried fish crackers with the humidity adsorbent also decreased after humidity testing, whereas the crispness of control decreased gradually. Furthermore, the humidity adsorbent has high sensitivity in reacting with humidity and maintain the crispness of fried fish crackers.

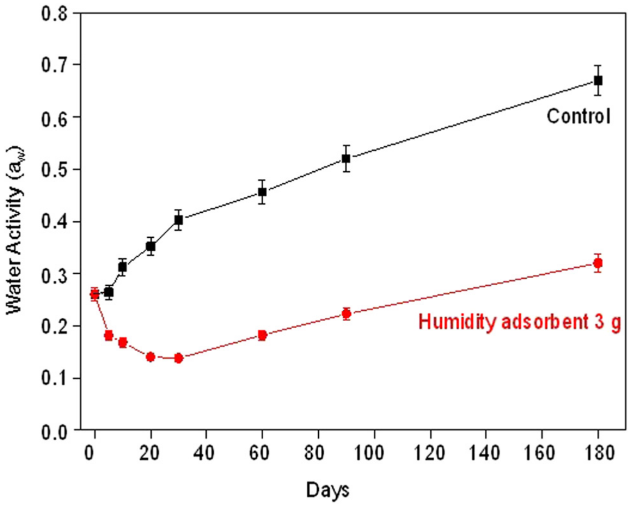

Figure 13: Water activity of fried fish crackers without humidity adsorbent (control) and with 3 g of humidity adsorbent for various humidity testing times.

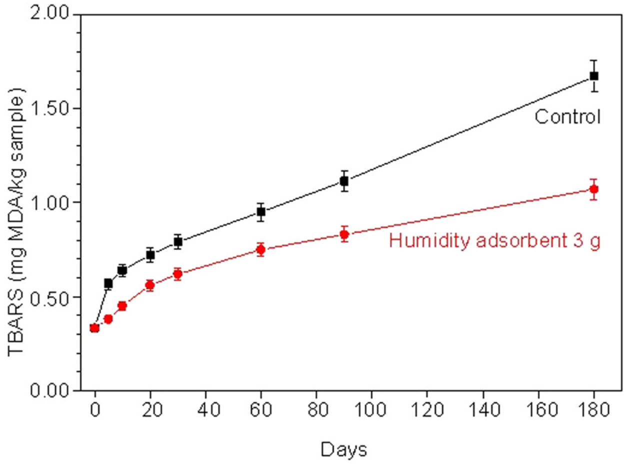

Figure 15: TBAS values of fried fish crackers without humidity adsorbent (control) and with 3 g of humidity adsorbent for various humidity testing times.

To support the potential for the humidity adsorbent from cockleshells, the rancid odor of the fried fish crackers was studied [40]. The TBARS values in all samples are shown in Figure 15.

The initial TBARS values (day 0) of fried fish crackers were about 0.29 mg MDA·kg^{-1} sample. The control in all periods of testing time shows the TBARS values in the range of 0.29–1.67 mg MDA·kg^{-1} sample. For 5 days, the TBARS values rapidly increased to 0.58 mg MDA·kg^{-1} sample. Because the initial packaging has oxygen molecules, the oxygen molecules immediately reacted with the lipid on the surface of the fried fish crackers [17]. After 5 days, the TBARS values gradually increased from 0.64, 0.72, and 0.79 mg MDA·kg^{-1} sample at 10, 20, and 30 days, respectively. This means that the oxygen concentration in packaging is low leading to the low reaction between lipids and oxygen. After 30 days, the TBARS values increased linearly to 0.95, 1.11, and 1.67 mg MDA·kg^{-1} sample at 60, 90, and 180 days, respectively. The tissue of fried fish crackers was damaged by the humidity or water molecules, resulting in the lipids in fried fish crackers easily reacting with the oxygen molecules due to lipid peroxidation [41]. While the fried fish crackers with the humidity adsorbent in all periods of testing time show the TBARS values in the range of 0.29–1.07 mg MDA·kg^{-1} sample. For 0–20 days, the TBARS value gradually increased from 0.29 to 0.56 mg MDA·kg^{-1} sample. The increase of TBARS in this range is affected by various mechanisms including the reaction of lipids with oxygen and humidity or water molecules in both the packaging and pores of fried fish crackers. However, the TBARS value of fried fish crackers with the humidity adsorbent is lower than that of the control. This is because the humidity or water molecules in the initial packaging were adsorbed by the humidity adsorbent resulting in low lipid oxidation. For 30–180 days, the TBARS values slightly increased from 0.62 to 1.07 mg MDA·kg^{-1} sample. At 180 days, the TBARS of the fried fish crackers with the humidity adsorbent had a low value of about 60% when compared with the control. The humidity adsorbent in packaging helps to adsorb humidity or water molecules and disrupt lipid oxidation.

Nevertheless, the general food has TBARS value in the range of 5.00–20.00 mg MDA·kg^{-1} sample [42]. For Thai food, the TBARS value should be less than 3.00 mg MDA·kg^{-1} sample, indicating that this food does not have a rancid odor [43,44]. Furthermore, the TBARS values at all times of fried fish crackers with and without humidity adsorbent show less than 3.00 mg MDA·kg^{-1} sample. Moreover, the TBARS results also related to the water activity results. All humidity testing results indicated that the humidity adsorbent from cockleshells can preserve the quality of fried fish crackers for at least 90 days.

4 Conclusions

The cockleshell waste was synthesized as the humidity adsorbent with the heat treatment process at approximately a temperature of 1,000°C for 4 h. XRD, FTIR, and SEM were used to characterize and confirm the crystal structure, functional group, and morphology of the humidity adsorbent, respectively. The cockleshell waste was mostly composed of calcium carbonate in the aragonite phase, which after the heat treatment process transforms into calcium oxide as a humidity adsorbent. The humidity adsorbent was applied to fried fish crackers during humidity testing for up to 180 days. After humidity testing of 30 days, the humidity adsorbent has high sensitivity in reacting with humidity and transforming into calcium hydroxide. At the same time, the fried fish crackers were studied for water activity, crispness, and TBARS. During the initial 30 days of humidity testing time, the values of water activity and crispness of fried fish cracker with the humidity adsorbent decreased, whereas the value of TBARS of fried fish cracker with the humidity adsorbent increased. After 30 days of humidity testing time, only the water activity value increased. Considering all the studied parameters, the humidity adsorbent from the cockleshells can maintain the quality of fried fish crackers for at least 90 days.

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