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Research Article

Synthesis and Characterization of Feed-Grade Monocalcium Phosphate $Ca(H_2PO_4)_2{\cdot}H_2O$ from Oyster Shell

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Oyster shells are considered as a byproduct or solid waste in mariculture or related food processing areas that face a major disposal problem at the landfill in coastal regions for sustainable development. Oyster shell is composed mostly of $CaCO_3$, and it is also considered as a secondary source of calcium for various applications. In this paper, we extracted the calcium carbonate from oyster shell and used it as the source of calcium for the preparation of feed-grade monocalcium phosphate (MCP). The investigation shows that the heavy metal contents in oyster shells as well as in the synthesized MCP are extremely low, and the synthesized product meets the requirements for the European Union (EU) maximum limits applied for feed additives. The XRD, TG, and IR data analyses confirmed that the synthesized product is monocalcium phosphate.

1. Introduction

Oyster shells are produced mainly in the mariculture and related food processing areas. After harvesting the oyster flesh, the oyster shells are mostly discarded as solid waste. In 2004, about 275,490 tons of oyster shells were produced, 70% of which were wasted in landfills or dumped into waters that may threaten the environment in water, culture medium, and land areas [1].

Various strategies have been proposed to face the problems, such as recycling of the shell wastes rather than disposal as the substitute for aggregate in mortar, building materials, plastic production, water and air treatment, and food supplements [2, 3]. Some others used oyster shells as an alternative calcium source for calcium carbonate instead of natural limestone [1], or the preparation of calcium hydrophosphate, monocalcium phosphate monohydrate, or tricalcium phosphate [4, 5]. In these investigations, the oyster shells are mixed with phosphate species to form the target materials without any proper purification so that most of the impurities, if any, in the starting materials will be retained in the final product.

The use of oyster shells as the calcium source instead of natural calcium carbonate for the preparation of feed-grade calcium phosphate will be interesting and fruitful. The oyster shells which contain a very low content of heavy metals, are generated by living animals, so they are more compatible to the animals as feed supply or additives [6]. The use of oyster shells for the preparation of feed-grade calcium phosphates will add significant value to the waste of mariculture as well as related food processing of bivalve shells.

2. Materials and Methods

2.1. Materials and Reagents. Oyster shells are collected from the Quang Ninh area, on the northeastern seacoast of Vietnam. After rubbing and cleaning with water, the samples are dried and ground to pass through a 160 μm sieve. Phosphoric acid of technical grade is supplied by Duc Giang Chemicals Group. All other chemicals used for the

experiments are reagent grade and commercially available and are used as received without any further purification.

2.2. Preparation Procedure. The precipitated calcium carbonate (PCC) is first prepared from the oyster shell by the modified procedure which is briefly described as follows [7]: the ground oyster shell is heated at 1000°C for 1 h, after cooling to room temperature, the powder is dispersed into water to get a hydrated lime slurry which is then filtered and the hydrated lime solution is bubbled with a flow of carbon dioxide gas until the pH of the formed slurry is about 7.0. The slurry is then filtered and washed with water, then dried at 105°C until the weight remains unchanged to obtain the PCC. The yield of the PCC has not been determined in the experiments.

The monocalcium phosphate monohydrate is prepared from the PCC and phosphoric acid [5, 8]. A typical example can be illustrated as follows: 100 g of phosphoric acid, 85.44% H_3PO_4, were diluted into 70.9 g of water to get a solution of 50% H_3PO_4, and then the obtained solution was heated to 90°C in a water bath. Then, 43.8 g of the precipitated calcium carbonate is gradually added into the solution in small portions, and the slurry was stirred continuously for about 1 hour to form a homogeneous mixture. The product was dried at 95°C to a constant weight and 109.8 g of white powder was obtained. The yield is almost quantitative.

2.3. Analytical Methods. The content of some trace elements such as As, Pb, and Cd in raw materials as well as in the synthesis samples is measured with inductively coupled plasma optical emission spectroscopy (ICP-OES) on Optima 8300 equipment (PERKIN ELMER). The samples with a weight of about 500 mg are added to an excess amount of nitric acid solution and diluted into 50 mL. For the quantification of the elements, an external calibration using the PERKIN ELMER multielement standard, so called *Quality control 21* solution (100 mg/L; 5% HNO_3) was employed. The mass concentrations of the standard solutions were 0 mg/L, 0.2 mg/L, and 1.0 mg/L. To recognize potential spectral disruptions, two different characteristic emission wavelengths were determined for every element, As: 193.696 nm and 188.979 nm; Pb: 220.353 nm and 217.000 nm; and Cd: 228.802 nm and 214.440 nm [9].

The calcium content in the samples is determined by the complexometric method with an ethylenediaminetetraacetic acid standard solution. The phosphorus content is measured by the vanadomolybdophosphoric acid colorimetric method on a Thermo Scientific SPECTRONIC 20D + spectrophotometer at a wavelength of 470 nm using KH_2PO_4 (99.5%, Sigma-Aldrich) as the standard for calibration [10].

The crystal structure of the samples was measured on a Rigaku MiniFlex600 diffractometer using a Cu anode for X-ray generation, $\lambda(\text{CuK}\alpha) = 1.54056$ Å, recorded at room temperature, scanning rate of 2.0°/min, recording intervals of 0.020°, with the two theta angles from 5° to 90°. The morphology of particles in the samples is evaluated with a scanning electron microscopy (SEM) on a Nova NANOSEM 450 equipment.

The thermogravimetric analysis (TG and DTG) of the synthesis samples is measured on a Setaram Labsys Evo S60/58988 (France) thermal analyzer. The sample, with an initial weight of 7.11 mg, is put on an alumina crucible and heated from room temperature to 850°C at a heating rate of 10°C/min, under the flow of air at a flow-rate of 20 mL/min. The weight and heat flow of the sample are recorded during the heat treatment.

The functional groups of the synthesis samples are investigated with FTIR measurements. A small amount of the sample is mixed with KBr, then pelletized (Pike), and scanned in transmission mode on a Jasco FTIR-4200 series spectrophotometer over the wavenumber range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}. The blank sample is pure KBr.

3. Results and Discussion

3.1. Composition and Characteristics of Oyster Shell, PCC, and the Synthesized Product. The composition of the raw materials for the preparation of the feed-grade additives is crucially important, not only the main ingredient but also the content of the impurities, especially the one of heavy metals which must be lower than certain levels [11, 12].

The X-ray diffraction analysis shown in Figure 1(a) and Figure S1 in the Supporting Information (SI) indicated that the $CaCO_3$ in oyster shell has a calcite structure (JCPDS No. 86-0174) which is in good agreement with other observations [2, 13].

The chemical analysis results show that the calcium carbonate content in the oyster shell sample is about 95.61% which is very close to the reported value of 95.994% $CaCO_3$ for the oyster shell [15]. The thermogravimetric analysis of the oyster shell sample is given in Figure 2(a).

The TG analysis in Figure 2(a) shows the weight loss of 44.58%, which is slightly higher than the expected value of 42.07% for the decomposition of a sample containing 95.61% $CaCO_3$. This may be ascribed to the decomposition of a small amount of organic matter in the oyster shell [16].

In order to investigate the potential applications of oyster shell as a material for the preparation of feed additives, the content of heavy metals including As, Pb, and Cd has been measured with ICP-OES. The results of the determination are shown in the Figure 3(a).

The results in Figure 3(a) show that the dilutions (10-fold) of the samples were measured, and the resulting values were found below the detection limit for these heavy metals. It means that the contents of As, Pb, and Cd in the samples are extremely small. Hence, the upper limits for the contents of these elements were evaluated from the limit of detection (LOD) in the measurement, and the results of the evaluation are shown in Table 1.

For oyster shell, the average upper limits for contents of As, Pb, and Cd are smaller than 27.1, 18.1, and 1.8 ppm, which are also lower than the European Union (EU) maximum limits of 30, 20, and 10 ppm, respectively, for feed additives [11, 12]. It means that the oyster shell meets the EU

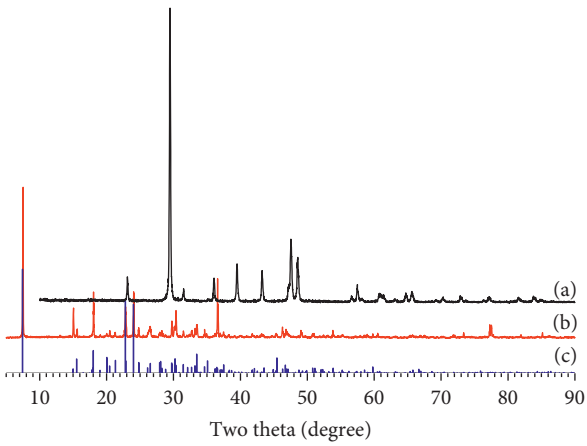

Figure 1: The XRD powder patterns of oyster shell (a), synthesized product (b), and the simulated one of $Ca(H_2PO_4).H_2O$ (c, JCPDS No. 71-0656) represented by the vertical bars, adapted from [14].

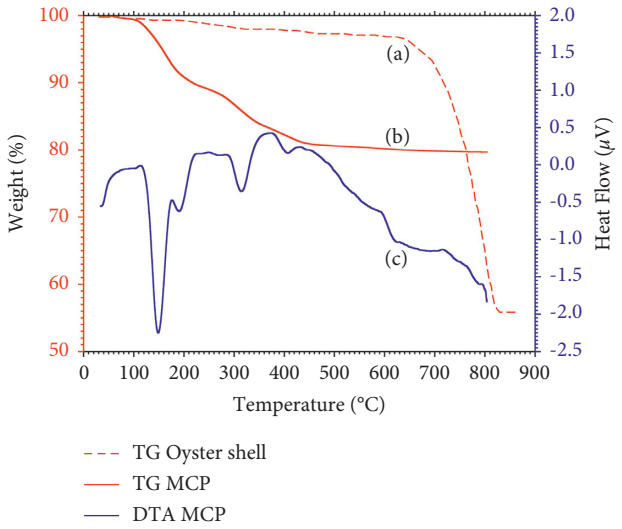

Figure 2: The thermogravimetric analysis (TG, red) and differential thermal analysis (DTA, blue) for the oyster shell (dotted curve, (a)) and the synthesized product (solid curve, (b) and (c)).

requirements for the content of heavy metals in applications or raw materials for the preparation of feed additives.

It is noted that oyster shell also contains some insoluble impurities that cannot be dissolved in nitric acid, even a concentrated one. The investigation shows that the content of the insoluble impurity is about 1.94%, and the XRD analysis indicates that it contains mostly SiO_2 (quartz, JCPDS No. 87-2096) and Al_2O_3 (corundum, JCPDS No. 85-1337), as shown in Figure S2 in the SI. The presence of these impurities may be unwanted for the materials needed to prepare the feed-grade additives like the MCP, so the purification of the oyster shell is required. The purification procedure of the oyster shell is described in Section 2.2 for the transformation of oyster shell into the PCC. The obtained PCC dissolves completely in dilute nitric acid (1 M), and the content of $CaCO_3$ in PCC is about 99.5%. The content of heavy metals in PCC has also been determined, and the results are given in Figure 3(b) which are also found beneath the detection limit for these heavy metals. The evaluated average upper limits for the contents of As, Pb, and Cd are smaller than 26.8, 17.8, and 1.8 ppm, respectively, which are also lower than the European Union (EU) maximum limits. Hence, PCC is a more suitable and preferred material for the preparation of feed-grade additives like MCP. The procedure for the preparation of the MCP is described in Section 2.2.

The chemical analysis of the synthesized product shows that the Ca and P contents in the sample is 15.80 and 24.63%, respectively, which is very close to the values of 15.86 and 24.60% for Ca and P as calculated from the $Ca(H_2PO_4)\cdot H_2O$ formula. The contents of the heavy metals in the synthesized product are also determined, and the results are shown in Figure 3(c).

The results in Figure 3(c) show that the contents of these heavy metals were also extremely small and found below the detection limit. The evaluation results for the upper limits for the content of these elements are given in Table 1. The evaluated average upper limits for the contents of As, Pb, and Cd are also lower than 26.8, 17.8, and 1.8 ppm, respectively, and these values are also smaller than the European Union (EU) maximum limits for feed additives. It means that the preparation of the MCP form PCC derived from oyster shell gives the synthesized product a very small content of heavy metals, and it is suitable for using as a feed additive.

3.2. Crystal Structure of the Synthesized Product. In the system of $CaO\text{-}P_2O_5\text{-}H_2O$, various phosphate phases and species may exist depending on the composition and conditions for the preparation. The structure of the phase(s) formed can be evaluated with the X-ray diffraction (XRD) which may be used as the fingerprint for phase analysis. The XRD patterns of the synthesized sample (b) and the simulated one based on the data of B. Dickens and J. S. Bowen (c, JCPDS No 71-0656) [14] are shown in Figure 1.

The XRD data in Figures 1(b) and 1(c) show that the powder pattern of the sample is consistent with the one of $Ca(H_2PO_4)_2\cdot H_2O$ which contain both Ca and P as confirmed by chemical analysis. Hence, the XRD measurement confirms that the synthesized product is a single phase of $Ca(H_2PO_4)_2\cdot H_2O$ as there are no additional peaks for other phases in the range of measurement.

3.3. Themogravimetric Analysis of the Synthesized Product. The thermal behaviour of the synthesized product can be investigated by thermogravimetric measurement. The TG and DTA patterns of the product are given in Figures 2(b) and 2(c) which show the relative weight and the heat flow of the sample when it is heated from 30 to 800°C. The thermogravimetric analysis data can be divided into different steps corresponding to the decomposition of the MCP and the elimination of water molecules from the sample. Before 100°C, the weight of the sample is almost unchanged and the absorbed water may be small. The weight loss of sample from 100 to 175°C is 7.20% which is close to the value of 7.14% as calculated for the elimination of one lattice water molecule

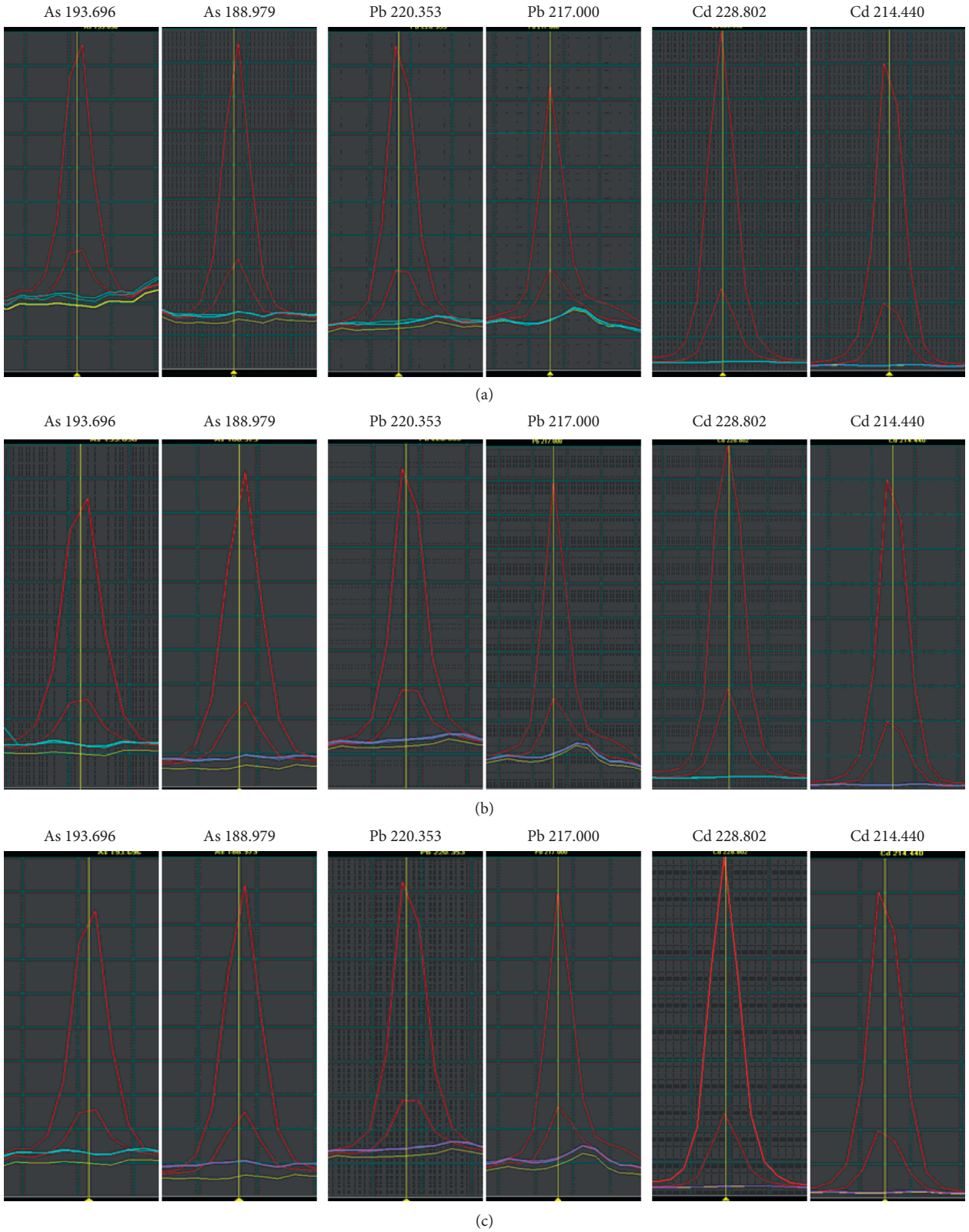

Figure 3: Emission spectra of the 10-fold dilution (turquoise/violet curves) of the oyster shell (a), PCC (b), and MCP (c) samples. The spectra of As are on the left, Pb in the middle, and Cd on the right. The yellow curves for the blank, and the red ones for calibration curves.

Table 1: Upper limits for the As, Pb, and Cd contents in the solid samples derived from the LOD in the solutions.

Sample	Content of heavy elements (ppm)					
	As (188.979 nm)	As (193.696 nm)	Pb (217.000 nm)	Pb (220.353 nm)	Cd (214.440 nm)	Cd (228.802 nm)
LOD, mg/L[(a)]	0.0217	0.0319	0.0064	0.0293	0.0016	0.0020
Oyster shell	<21.9	<32.3	<6.5	<29.7	<1.6	<2.0
PCC	<21.7	<31.9	<6.4	<29.3	<1.6	<2.0
MCP	<21.7	<32.0	<6.4	<29.3	<1.6	<2.0

[(a)]The LOD in the measured solutions is evaluated from the standard deviation (σ) of the blank measurements, LOD = $3 \times \sigma$.

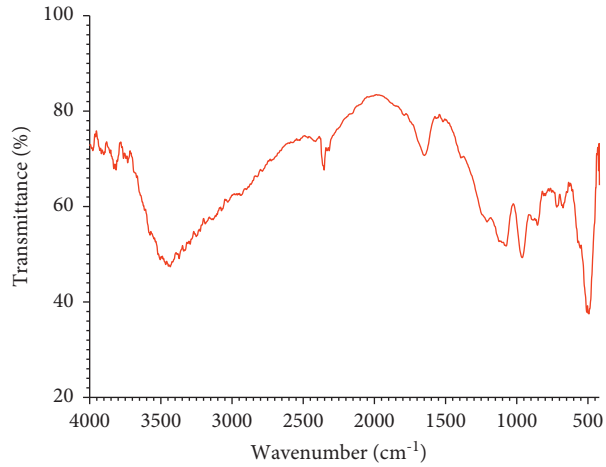

Figure 4: The FTIR spectrum of the synthesized product.

per formula unit of $Ca(H_2PO_4)_2 \cdot H_2O$ as an indication of the large endothermic peak at 150°C on the DTA curve. On further heating, the weight loss of the sample when heated from 175 to about 700°C is 13.80%. The observed value of weight loss is rather close to the value of 14.28% for the removal of 2 water molecules from the intermediate of calcium dihydrogen phosphate to $CaH_2P_2O_7$ and then to stable calcium metaphosphate, $Ca(PO_3)_2$. The decomposition of $Ca(H_2PO_4)_2$ as well as the one of $CaH_2P_2O_7$ is also endothermic, as showed in the corresponding DTA curve. The overall reaction for the thermal decomposition of MCP can be represented by the following equation:

$$Ca(H_2PO_4)_2 \cdot H_2O \longrightarrow {}^{150^\circ C}Ca(H_2PO_4)_2 + H_2O \longrightarrow {}^{200^\circ C}CaH_2P_2O_7 + 2H_2O \longrightarrow {}^{300-500^\circ C}Ca(PO_3)_2 + 3H_2O \quad (1)$$

So, the results of thermogravimetric data analysis confirm that the synthesized product is calcium hydrogen phosphate monohydrate [8].

3.4. The Infrared Analysis of the Synthesized Product. The expected product contains some functional groups, and their presence in the sample can be confirmed by infrared spectroscopy measurement. The Fourier transformation infrared (FTIR) spectrum of the synthesized product is given in Figure 4.

The FTIR spectrum in Figure 4 is rather close to the one reported somewhere and confirms the presence of lattice water molecules as well as the phosphate species in the sample [17]. The observed bands can be assigned as follows:

The broad band centered at 3440, the small bands at 2350 and 1650, and the one at 670 cm^{-1} are assigned for the O-H stretching, the H-O-H rotation, bending, and rocking modes of the lattice water molecules in the monocalcium phosphate monohydrate, respectively.

The small band at 1200 cm^{-1} is ascribed for the P-O-H in-plane bending, and the bands at 950 and 1070 cm^{-1} are for the P-O stretching. The band at 850 and the one centered at 500 cm^{-1} are assigned for the P-O (H) stretching and bending, respectively.

3.5. The Particle Morphology of the Product. The particle morphology of the synthesized product is evaluated with scanning electron microscopy (SEM) measurement. The typical image measured at a magnification of 500 times is shown in Figure 5.

The results in Figure 5 show that particles with a parallelogram-like shape were obtained, which is in good agreement with the results of other work [8].

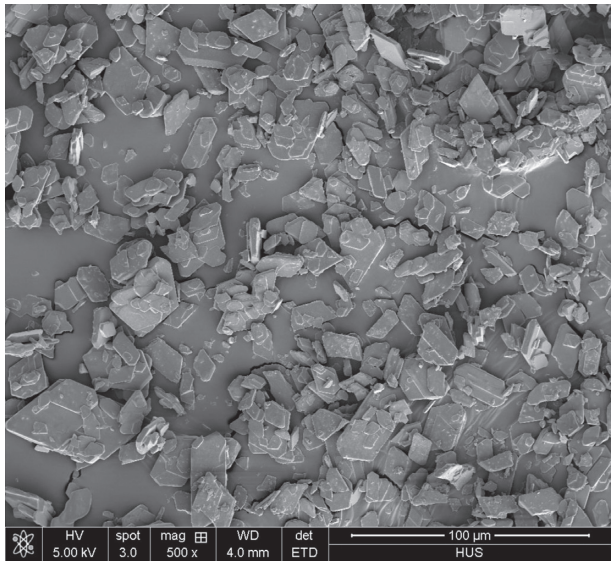

Figure 5: The SEM image of the synthesized product.

Most of the particles are rather small, with a size of about 10–20 μm in length, 5–10 μm in width, and a thickness of a few microns. Small particles may make the dispersion of the product become easier and form more homogeneous ingredients when it is used as feed additives.

4. Conclusions

Oyster shells sometimes are solid waste in mariculture or related food processing areas that face a major disposal problem in coastal regions. Oyster shell also contains a high content of $CaCO_3$ with low content of heavy metals, and it can be recycled and used as a secondary calcium source for the preparation of high-value materials such as feed additives like MCP. The transformation of oyster shell into PCC will remove certain impurities to obtain high quality starting materials for the preparation of MCP. The contents of the heavy metals such as As, Pb, and Cd in oyster shell, PCC, and the synthesized product are all extremely low, and the evaluated values are smaller than the EU maximum limits for feed additives. The synthesized product contains a pure phase of monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2{\cdot}H_2O$, as confirmed by the XRD data, TG, or chemical analyses.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this study.

Acknowledgments

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Supplementary Materials

Figure 1: the powder X-ray diffraction patterns of the oyster shell (black lines) and the simulated ones of calcium carbonate in the calcite modification (blue lines) adapted from JCPDS No. 86-0174. (S1) The observed XRD powder pattern of the oyster shell is similar to the calcite form of $CaCO_3$. Figure S2: the X-ray diffraction patterns of oyster shell residue after digestion with nitric acid. The green vertical lines represent quartz (SiO_2, JCPDS No. 87-2096), and the red lines represent corundum (Al_2O_3, JCPDS No. 85-1337). (*Supplementary Materials*)

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