REUSE OF WASTE CRAB SHELLS FOR SYNTHESIS OF CALCIUM CARBONATE AS A CANDIDATE BIOMATERIAL

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ABSTRACT
The crab shell (Portunus Pelagicus) wastes are constituted of major calcium carbonate (account for 70 wt. %) and have the potential to reuse as a starting biomaterial for precipitated calcium carbonate (PCC) products. The purpose of the present work was to synthesize PCC powder using crab shells based on the gas-solid-liquid carbonation route. In this experiment, crab shell powder was prepared by washing, drying, and subsequent grinding. The resulting powder was then calcined at 900 ℃ for 5 h before being used for the synthesis of the PCC product. Later, the calcined crab shell powder was dissolved with 2M HNO₃ solution in a glass beaker with the pH solution of 12 set up by adding NH₄OH. The solution was subsequently stirred magnetically for 30 min. The carbonation process ended when the PCC solid was obtained at a pH of 7. The crab shell powder, crab shell powder after calcination, and the obtained PCC solid were then characterized using XRD, SEM-EDX, and FTIR methods, respectively. The resulting PCC product has been shown to have calcium carbonate with the major vaterite phase. This experimental work demonstrated the potential application of crab shells for a low-cost biomaterial of future medical applications.

Keywords: Crab Shell, Precipitated Calcium Carbonate, Portunus Pelagicus, Calcium Carbonate

INTRODUCTION
Crab shells are found as abundant renewable, inexpensive biological wastes in the Indonesian seafood industry. The Ministry of Marine Affairs and Fisheries of the Republic of Indonesia, reported on January 21, 2020, that at least 161 tons of crabs (without shells) could be produced from the Fish Processing Unit (UPI) located in Demak and Rembang Regency, Central-Java Province. If the crab shells represent 25%-50% of the total crab weight¹, then the total waste crab shells are equal to 81 tons. In addition to the high calcium carbonate content, accounts for 40-70 wt. %, these high amounts of waste materials have the potential to be reused as a low-cost raw biomaterial for the synthesis of precipitated calcium carbonate (PCC). Instead, these biological wastes provide benefits on environment-friendly raw biomaterials, which can be employed for synthesizing chemically calcium orthophosphate bioceramics.² Recently, the waste crab shells have been reused as resources for chitin and chitosan, drug delivery systems, and removing metals from aqueous solutions.³–⁶ Also, the synthesis of biomaterials such as hydroxyapatite (HAp) [Ca₁₀(PO₄)₆(OH)₂] or carbonated hydroxyapatite (CHAp) powders employed of PCC product of the processed shells powders.⁶ These apatite powders derived from crab shells have been shown to have similar chemical compounds to those of human bones and have good biocompatibility with bones. For this reason, a bone treatment with those powders has been successfully implemented for autologous bone grafting, which has become the standard of bone defect repair due to its biological advantages of being estrogenic, osteoinductive, and osteoconductive.⁵,⁷–⁹

In view of the economic value of waste crab shells, efforts have paid much attention to reuse as a starting biomaterial in developing PCC products. In particular, using the aqueous crystallization process for treating these wastes provides the beneficial crystalline calcium carbonate with controlled morphology.⁹ Three types of calcium carbonate may be formed in anhydrous polymorphs, namely calcite, aragonite, and vaterite with different morphology depending on the synthesis conditions.¹⁰,¹¹ With rhombohedral crystals, calcite is most stable and commonly used for the sustained and targeted release of the drug into cancer cells.¹³ Additionally, aragonite with an orthorhombic crystal could be formed at high pressure to
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have good biocompatibility, thereby applying for the human bone implant.\textsuperscript{13,15} This mineral has long been implemented for carriers of anticancer drugs and scaffolds for bone repair and tissue engineering.\textsuperscript{14}

Among the third form of calcium carbonate, the lowest stability of phase is vaterite with the hexagonal crystal structure. However, in contact with air, it can recrystallize to a stable form.\textsuperscript{15} Having high porosity and surface area and decomposing rapidly in relatively mild conditions, vaterite becomes an ideal candidate for various medical applications. It is also an important component used actively in bone implants, abrasives, cleaners, and absorbents, along with the encapsulation and delivery of drugs, medicine.\textsuperscript{10,14}

Because of the extensive applications of PCC products in biomedical engineering with particle sizes below 1\textmu m, the synthesizing method of PCC has become an interesting research topic. Correspondingly, waste crab shells could be exploited by a chemical precipitation method to yield PCC powder. Here the PCC product could best be synthesized by flowing CO\textsubscript{2} through a containing calcium slurry with a suitable pH solution. It was demonstrated previously that the solid-liquid reaction method was a suitable method for synthesizing PCC from biological resources.\textsuperscript{16,17}

The purpose of the present work was to reuse crab shell wastes for making PCC products through laboratory powder processing methods including grinding, calcination, and carbonated precipitation processes. The ground, calcined, and PCC powders of crab shells were further subjected to material characterizations (XRD, SEM/EDX, and FTIR methods) to investigate their mineralogical phase compositions and morphology of the sampling products. The result is expected to add knowledge of the powder processing strategy of the crab shell wastes for preparing PCC products with good purity and specific morphology.

EXPERIMENTAL

Material and Methods

The waste crab shells were received from the Rembang area, located in Central Java Province, Indonesia. This waste was subsequently processed for powder synthesis as shown in Fig.-1. The powder processing methods included washing the waste with clean water and drying it under the sun. The dried crab shells were then crushed in a blender, and the resulting powder was filtered with 100 mesh. Subsequently, the calcination of this powder was performed at the 900 °C for 5 h within a furnace (Carbolite\textsuperscript{R}). Eventually, all powder samples were subjected to characterization by XRD, SEM-EDX, and FTIR methods.

![Fig.-1: Powder Processing Method of the Waste Crab Shells](image)

The experimental procedures for making PCC products are shown in Fig.-2. In this method, the calcined powder (17 g) was initially dissolved in 300 ml of 2M HNO\textsubscript{3} to prepare the crystal-forming solutions with a pH of 12. These solutions were stirred magnetically at 60 °C for 30 min. Before the mixed solution was carbonated, the filtration was performed in a glass flask equipped with filter paper (Whatman@42) and ended when pH was 7. Later, the CO\textsubscript{2} gas was slowly injected into the filtrate to yield the precipitating solids of the PCC product. The precipitating solid was separated with filter paper and the obtained slurry was dried at 110 °C in the oven for 2 h. The dried PCC product was subjected to subsequent material characterizations by XRD, SEM-EDX, and FTIR methods.
Further XRD method examined the received XRD data of specimens by search-matching of peak positions and peak intensity with the JCPDS (joint committee on powder diffraction standards) database. The XRD Rietveld method (FullProf-2k software version 3.30) based on the AMCSD (the American mineralogist crystal structure database) model justified the matched-phase identifications. Instead, all powder samples obtained during the study were observed for morphology through a scanning electron microscope (SEM, FEI Inspect S50). Its morphology in conjunction with the XRD intensity was eventually analyzed and discussed. Moreover, FTIR spectrometry (IR-Prestige88) operating at 200 scans/s with a spectral of 2 cm\(^{-1}\) resolution, collected compound data of the sampling PCC product with all spectra at bands from 400 to 4000 cm\(^{-1}\).

**RESULTS AND DISCUSSION**

Chemical elemental analysis based on SEM-EDX data for received crab shells, calcined crab shell powders, and the PCC powder is presented in Table-1. Apparently, the crab shell powder contains major elements (% mass) of 24.49 % Ca and 29.44% C in addition to Na, Mg, P, and Zr impurities of 0.38 %, 1.40 %, 3.33 %, and 1.99 %, respectively. After the calcination process of the ground samples, the Ca level enhanced, while the reduced C content could be noted. During calcination, calcium might decompose to yield C binding O for CO\(_2\) gas formation, whereas Ca was oxidized to form CaO. Moreover, at a calcination temperature of 900 °C, there were still impurities of Na, Mg, Al, P, and Cu namely 0.58%, 3.89%, 0.17%, 2.98%, and 1.08% respectively. However, the PCC powder has a decreased Ca level due to carbonation for CO2 formation. These corresponding chemical elements to the phases formed in the observed samples were then justified by the XRD method (Fig.-3).

<table>
<thead>
<tr>
<th>Element (% Mass)</th>
<th>Received Crab Shell Powder</th>
<th>Calcined Powder</th>
<th>PCC Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>29.44</td>
<td>7.38</td>
<td>15.43</td>
</tr>
<tr>
<td>O</td>
<td>38.97</td>
<td>47.99</td>
<td>54.44</td>
</tr>
<tr>
<td>Na</td>
<td>0.38</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>24.49</td>
<td>35.94</td>
<td>17.56</td>
</tr>
<tr>
<td>Mg</td>
<td>11.4</td>
<td>3.89</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>3.33</td>
<td>2.98</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>1.99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>1.08</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>-</td>
<td>12.57</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure-3 shows analysis results of the XRD data on the raw, calcined powders of the crab shells and PCC samples. Moreover, the XRD Rietveld analysis of the crystalline phase confirmed phases formed in the raw and calcined powder and PCC samples (Table-2). In the raw powder sample, the highest intensities of
XRD peaks could be observed at 2θ° of 29.4, 39.3, and 43.1, respectively. These peak intensities correspond to calcite according to JCPDS#05-0453. The calcined powder samples obtained at a temperature of 900 °C showed the highest intensity peaks at 2θ° of 18, 34.1, and 50.7 corresponding to the phase formation of portlandite [Ca(OH)\(_2\)] according to JCPDS#44-1481. In contrast, the highest XRD peaks could be noted on the PCC sample at 2θ° of 24.9, 27.07, and 32.7, corresponding to vaterite according to JCPDS#13-0192. In addition, there are crystalline phases of calcite and aragonite found on the PCC samples according to JCPDS#05-0586 and 05-0453. Presumably, the formation of vaterite related to the increasing flow rate of CO\(_2\) gas, which made an increase in its solubility within the solution. 

![Fig.-3: XRD Diffractograms of Raw Crab Shell, calcined Powders, and PCC Product](image)

Table-2: The Crystalline Phase of Raw Crab Shell, Calcined, and PCC Powders

<table>
<thead>
<tr>
<th>Crystalline Phase</th>
<th>Raw Crab Shell Powder</th>
<th>Calcined Powder</th>
<th>PCC Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Aragonite</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Vaterite</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Portlandite</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

In this experimental work, the phases formed in the samples could be related to their morphologies which were observed by SEM examination. Fig.-4 presents the observed morphology of crab shell powder, calcined powder, and PCC. The raw crab shell powder has an irregular-shaped morphology with small size particles (< 5 µm), while the branched stems, which are characteristic of aragonite crystals, could be observed in the SEM image (Fig.-4a). This result is consistent with that reported by Pacton et al\(^{16}\). Moreover, morphology observed in the calcined powder sample has a non-uniform hexagonal shape (Fig.-4b). This feature may relate to two phases formed in the calcined powder sample. The hexagonal shaped-morphology of portlandite (Fig.-4c) could be observed in the sample during the study, which is following the result of research conducted by Jiang et al.\(^{17}\) Additionally, the PCC product has a uniform spherical shaped-morphology, which is related to vaterite.\(^{18}\)

Further results of calcium carbonate compounds observed by the FTIR method are shown in Fig.-5. Table-3 summarizes the bonds that exist in the raw crab shell powder, the crab shell powder after calcination and PCC powder. It shows that calcium carbonate compounds could be characterized based on the peaks appearing in the FTIR spectrum. The raw crab shell has a peak at a wavenumber of 1400-1500 cm\(^{-1}\), corresponding to the presence of a C-O bond, which is a typical spectrum of carbonate compounds. Additionally, the FTIR spectra of the PCC sample have a relatively low peak appearing at the wavenumber around 3400-3600 cm\(^{-1}\) that relates to the presence of an O-H bond. Evidently, the results of the FTIR spectra from PCC provided the identified vaterite. In this case, vaterite could be characterized by the presence of a sharp peak at a wavenumber of 879 cm\(^{-1}\).\(^{17}\) The presence of an OH group related to
Ca(OH)$_2$ with a sharp level around 3641 cm$^{-1}$ may have come from water molecules that were absorbed on the surface of CaO, where CaO is hygroscopic and easy to absorb water from its surroundings. Correspondingly, portlandite could be used as the starting material for vaterite with controlled morphology and be also employed in Portland cement matrices.

**Fig.- 4:** SEM Images (a) Crab Shell Powder; (b) Calcined Crab Shell Powder; (c) PCC Powder

**Fig.- 5:** FTIR Spectrum results of Raw Crab Shell, calcined Crab Shell, and PCC Powders

**Table-3:** Results of the FTIR Spectra for each Powder Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>C–O Bond (1400-1500 cm$^{-1}$)</th>
<th>O–H Bond (3400-3600 cm$^{-1}$)</th>
<th>Ca–O Bond (700-900 cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw crab shell powder</td>
<td>1436.11</td>
<td>3430.19</td>
<td>874.04</td>
</tr>
<tr>
<td>Calcined crab shell powder</td>
<td>1458.14</td>
<td>3642.74</td>
<td>871.82</td>
</tr>
<tr>
<td>PCC powder</td>
<td>1474.25</td>
<td>3446.16</td>
<td>875.76</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The study demonstrated that the PCC powder could be synthesized from the reuse of the waste crab shell powder. The PCC powder has aragonite, calcite, and vaterite with uniform morphology characteristics, as justified by XRD, SEM-EDX, and FTIR methods. Evidently, C-O and Ca-O group bonds that are characteristic of calcium carbonate contents could be confirmed by FTIR analysis. The phases and morphology formed in the PCC products are mainly related to the effect of the carbonation process. This PCC product could be a candidate starting biomaterial for further synthesis of a typical crystal form of calcium carbonate polymorph.
ACKNOWLEDGEMENT
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