Characterization of Morphological and Crystal Structure of Coral Reefs Samples from Depapre District, Papua

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Abstract. There are concern about a massive volume of unused and dead coral reefs that lie along the coastline in Depapre district, Papua Province. The application of this natural waste is strictly limited due to lack of public knowledge about the advantage of this material for any purposes. This study aims to determine the potential application of unused and dead coral reefs by characterizing their morphology and its crystal structure. One of the major advantages of this study is to find out whether this material can is suitable to use as basic material in synthesis of hydroxyapatite. There are three types of coral reefs that obtained from the area, including Acropora cervicornis, Porites mayeri, and Pocillopora damicornis. These three types of coral reefs were characterized to determine their crystal structure using X-Ray Diffraction (XRD) and their morphological shape by using a digital microscope and Scanning Electron Microscope (SEM). The characterization procedure was carried out before the calcination process and after the procedure at a temperature of 1000°C. This study have found that the samples had different size in terms of pores. Prior to the calcination process, all samples showed a single phase that consist of calcium carbonate (CaCO₃) in the structure form of Aragonite crystal. After the calcination procedure, the crystal structure was shifted to Calcite and it was also decomposed to CaO. The particle size of the reef powder was much smaller in volume and it was more homogeneous after it went through the calcination process, in which it ranges from 3 μm to 5 μm.

1. Introduction

Indonesia is geographically the largest archipelago state in the world, where the total area is 7,81 million square kilometers, that consist of 3.2 million square kilometers of coastline [1-4]. The characteristics of this vast marine area provide the country with abundant biodiversity from marine resources, one of which is the natural coral reef that lies across the ocean bed for many years [5, 6]. The coral reef is crucial for the economic sector as it supports the sustainability of marine ecosystems, which is important on supporting the preservation of fishery resources, and it is useful for protecting the water areas from erosion, as well as the negative impacts that caused by large waves [7, 8].

Scientifically, coral reefs have massive deposits of calcium carbonate (CaCO₃) that produced from coral animals, with the additional of calcareous algae and other organisms that capable to produce calcium carbonate [9, 10]. Although some of the reef ecosystem in Indonesia is quite well preserved as a result of various conservation efforts from the Government and the NGOs [11, 12], there are findings that over two thirds of the reefs have been reported to be decolorized or dead [13, 14]. Scientist found that the
damage coral reefs are the impact of various activities such as earthquake or unsustainable fishing activities\textsuperscript{[5, 15, 16]}. One of the biggest cases of damage coral reefs in Indonesia, is in the Depapre District, Jayapura Regency. It is the eastern part of the country in Papua Province. In the past, this area was a productive fishing area that inhabited by various species of fish \textsuperscript{[17]}. At the present time, local fish production from Depapre has been declined along with the destruction of local coral reefs \textsuperscript{[18, 19]}. This impact can be seen from the frequent remnants of the reefs that washed up by the waves to the shore. These dead reefs have become organic waste due to the lack of knowledge from local society about the use of it on their daily life. Only a small group of people in the area that process the reefs for consumption, particularly when they have makan pinang \textsuperscript{[20, 21]}. A local type of snacking to chew betel nuts, as it is believed to have good effect on healthier tooth and mouth. It is a traditional routine that have been passed through generations.

This paper attempts to contribute to enrich the utilization of dead and unused reefs for various applications. Considering the calcium carbonate content in the coral reefs can be extracted for its calcium content. It would be latter applied for various purposes in the health sector, for instance, on creating bio ceramics \textsuperscript{[22]}. One example of the use of calcium carbonate for medical application is to act as a basic material for hydroxyapatite manufacturing process. The hydroxyapatite is applicable as a calcium substitution for human bones and it can be used as a natural dental implant in oral surgery \textsuperscript{[23]}. However, in order to use this material, the hydroxyapatite needs to be synthesized. It is a process to convert CaCO\textsubscript{3} into CaO through the calcination method \textsuperscript{[24]}.

In order to determine the prospect of calcium content in dead reefs from Depapre district in Papua, this study attempt to identify the species of coral reefs in the region and to build its characterization from various types of the reefs that found in this research. The characteristics are referred to the morphological surface and the crystalized structure of the reefs. This study aims to provide initial information about the processing development of unused and dead reefs into hydroxyapatite.

2. Experimental Method
The main material that used in this study is dead coral which is obtained along the coastline of Depapre District, Jayapura Regency. The additional material which is used in this research is distilled water. The first stage is carried out to identify the types of species from dead coral reefs and to collect three different species of the reefs. These samples went through a cleaning stage to remove all organic residue from the coral surface.

After taking a photo of the morphological surface of the sample by using a digital microscope, the reef sample was crushed into powder and it was continued to the calcination stage. The calcination temperature was set to 1000°C. The characterization of reef samples was carried out before and after the powder was calcined. The tools that used in the characterization process until it turned into coral powder were x-ray diffractometer to investigate the crystalized structure of the sample. The process was then continued into scanning electron microscopy to take photos of the morphological surface of the sample.

3. Results and Discussion

3.1. Surface morphology characterization
From the identification process of coral reef species that found in Depapre District, there are three different types of coral reefs, as shown in Figure 1.
To determine the physical properties of coral reefs such as pore size and shape, a digital microscope is used to analyze them. From Figure 2. It is clear that the pore size is in the range of 83 $\mu$m - 818 $\mu$m.

Figure 2. Digital micrograph of three types of coral reefs found in Depapre District; (a) Acropora cervicornis (b) Pocillopora damicornis and (c) Porites mayeri.

The above figure is a photo that have been generated from SEM. This figure shows the surface of Porites mayeri powder before the sample was calcined and after the procedure has completed. The process reveals that the calcined reef powder is much smaller in terms of particle size and it is much more homogeneous. The particle size is ranging from 2 to 5 $\mu$m.

Figure 3. SEM morphological characteristics of Porites mayeri sample in a magnification of 2000$\times$; (a) before the calcination process (b) after the calcination process.

3.2. Crystal structure identification

According to data from the XRD analysis, the three types of coral reefs only show a single phase (JCPDS file No.76-606 was correspond to aragonite--CaCO$_3$). As it is shown in Figure 4. The three types of reefs show similarities in its chemical content, in which it consists of calcium carbonate (CaCO$_3$) in the form of aragonite crystal structure.
Figure 4. Diffractogram sample of three types of coral reefs powder

After the samples went through the calcination process, there were changes in crystal phase from CaCO$_3$ aragonite to CaCO$_3$ calcite. At the same time, some of the samples have decomposed into CaO. Transformation within the crystal phase is occurred because the CaCO$_3$ calcite is more likely to form at high temperature than the CaCO$_3$ aragonite. Temperature during the calcination process would determine the structural transformation in a material.

Figure 5. Diffractogram of the samples for three types of coral reef after the calcination process in 1000°C.
The XRD results for the species of reefs Acropora cervicornis and Pocillopora damicornis has shown similar dominance ratio between phases CaCO$_3$ calcite and CaO. However, the most dominant phase in Pocillopora damicornis was CaO. In Figure 4, it can be seen that the phase of CaO shows a diffraction pattern with the highest intensity that peak at $2\theta = 37.25$ and a decrease in the intensity of CaCO$_3$ calcite phase.

4. Conclusion
This study aims to characterize the unused and dead coral reefs from Papua to determine its feasibility to use as a basic material in the manufacturing process of hydroxyapatite. There are three samples that used in this study; Acropora cervicornis, Pocillopora damicornis and Porites mayeri. All types of the samples have different physical characteristics, in terms of the shape, size of the pores and its particle mass after the calcination process. The structure characteristic of the crystals have found that all samples have a crystal structure of CaCO$_3$ aragonite before it went through the calcination process. After the calcination procedures there was a shift in the crystal phase from CaCO$_3$ aragonite to CaCO$_3$ calcite, where at the similar process, some of the samples have turned into CaO as a result of decomposition. The SEM morphology photo shows that the calcination process has transformed the samples to more homogeneous form with smaller particle size. Therefore, this paper conclude that there is a positive prospect that unused and dead coral reefs would be applicable to create material for hydroxyapatite. This finding is highly valuable to provide preliminary data about the synthesis development of hydroxyapatite.

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