Protein and Minerals Analyses of Mangrove Crab Shells (Scylla serrata) from Merauke as a Foundation on Bio-ceramic Components

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Abstract. The analyses over protein and mineral content of mangrove crab shells from Merauke had been studied and then it is presented in this paper. The methods were started by cleaning the shells from impurities, then it naturally dried for 24 hours, and then it was grounded into form of powder. The results showed that the raw powder of mangrove crab shell was contained 19.78 % of Carbon (C), 24.53 % of Oxide (O), 4.81 % of MgO, 3.98 % of P2O5 and 71.42 % of CaO. The calcined process has succeeded to decrease the carbon content. The minerals content of the crab shells after it was calcined at 1000 °C were 6.27 % of Carbon, 28.96 % of Oxide, 5.78% of MgO, 5.65 of P2O5, and 82.3% CaO. Therefore, it can be concluded that the mangrove crab shells from Merauke possess basic materials as bio ceramic.

1. Introduction
Crab has been well known for its calcium rich content. Previous study from Parangipettai, India, reported that crab (Calappalophos) have calcium content of 2452 mg/kg in meat, and 2346 mg/kg in shell, yield total calcium content of 4798.0 mg/kg [1]. Another study from Badagry Creek, Nigeria reported that Callinectes pallidus and Cardisoma armatum crab have calcium content of meat were 3843.95 mg/kg and 18901.51 mg/kg respectively while the calcium content of shell were 3843.95 mg/kg and 18901.51 mg/kg respectively. However, each crab species has a different percentage of mineral content depending on its habitat. Scylla serrata (also called mud crab or mangrove crab) is a species of crab which generally found in the estuaries and mangroves of Africa, Australia and Asia [3]. This species of crab was considered as a high economically species due to its high production, more than 80 % of the total culture production of the world [4].

The high level of availability along with the consumption of crab consequently will increase the level of related waste, particularly the shell. This has encouraged research on utilization of crab shell, for examples as a catalyst in biodiesel [5] and chitin production process [6]. In this study, we enlighten the content of calcium in crab shell waste. Recently, calcium bio-ceramic utilized from waste sell has gain attention. Biocermic is an advanced ceramic material used in medical and dental industry, as implant or subtitute material. Some of which have been developed are Ca-hydroxyapatite from egg shell [7], calcium carbonate bioceramic from cockle shell [8], and calcium phosphate powders from marine shell [9]. Furthermore, bioceramic materials mostly synthesized using thermal method to increased the material quality and remove its impurities and organic materials [7].
Based on their calcium content described earlier, crab shells have considerable potential as the basic ingredients of bio-ceramic production. Therefore, this study is aimed to provide a preliminary study of mineral content that found in crab shell as the basic ingredient of bio-ceramic. We utilized Merauke mangrove crab, which is also abundantly presence in Indonesia, however no study related to its mineral content reported yet. Merauke mangrove crab shells (*Scylla serrata*) were selected since it came from natural ecosystems that are less polluted from urban and industrial activities, compared to other mangrove area in Indonesia. Moreover, it is highly abundant, easy to obtain in restaurant industrial in Indonesia, and considered as a waste for every household.

2. Materials and Methods
The crab shells used in this study were obtained from the mangrove areas in Merauke District, Papua, Indonesia. The collected shells were cleansed from macro impurities and subsequently natural dried for 24 hours. The cleaned and dried shells were crushed using a grinder to obtain a shell powder form. The raw powder (without any calcinations process) was divided into two parts. The first part used for protein and minerals content characterization, while the other part was calcined through various temperature of 800 °C, 900 °C dan 1000 °C for 5 hours at ambient process. Afterwards, the mineral content of the calcined samples were characterized to measure its mineral content.

The protein content of the raw shell powder were characterized Atomic Absorption Spectrophotometer (AAS). The mineral content for all samples was characterized using EDS (Energy Dispersive Spectroscopy) and the XRF (X- Ray Fluorescence).

3. Results and Discussions
The protein content of the mangrove crab shell from Merauke was analyzed by AAS method. The result revealed that the value reached up to 9.57 %. As a comparison, two species of crab from Badagry Creek, Nigeria, *Callinectes pallidus* and *Cardisoma armatum*, have protein content of shell of 21.45% and 24.38% respectively [2].

Figure 1. The EDS spectrum of crab shell powder (a) raw powder, without calcinations, (b) calcined at 800 °C, (c) calcined at 900 °C, and (d) calcined at 1000 °C.
Hereafter, we analyzed the mineral content through the EDS method. Figure 1 shows the EDS spectrum qualitative analysis of mineral from the shell (a) raw powder without calcinations, (b) powder calcined at 800 °C, (c) calcined at 900 °C, and (d) calcined at 1000 °C. It clearly seen that calcium was the dominant mineral in all samples.

Furthermore, figure 2 gives the quantitative analysis of mineral from the shell. It was calculated that the raw powder of mangrove crab shell was contained 19.78 % of Carbon (C), 24.53 % of Oxide (O), 3.98 % of P2O5 and 71.42 % of CaO. The calcination process has decrease the content of carbon, in contrast, increase the content of oxide [7], corresponds to a chemical reaction below.

\[
\text{CaCO}_3 \xrightarrow{\text{calcined}} \text{CaO} + \text{CO}_2 \uparrow
\]  

Before calcined, the calcium (Ca) in the shell were in compound of CaCO3, hereafter the calcination process the calcium compounds turned to CaO and evaporates CO2. Therefore, the calcinations process has yield the decrease of carbon.

![Figure 2. Mineral oxide quantitive analysis using ZAF method of crab shell powder (a) raw powder, without calcinations, (b) calcined at 800 °C, (c) calcined at 900 °C, and (d) calcined at 1000 °C.](image)

From the variation of calcinations temperatures, we can conclude that the optimum temperature which produced more pure CaO was 1000 °C. Minerals content of magrove crab shells after calcined at 1000 °C were 6.27 % of Carbon, 28.96 % of Oxide, 5.78% of MgO, 5.65 of P2O3, and 82.3% CaO. This value was comparable with the reported value from hen’s egg shells [10].

**Table 1.** The XRF results of of crab shell powder (a) raw powder, without calcinations, (b) calcined at 800 °C, (c) calcined at 900 °C, and (d) calcined at 1000 °C.

| Element | (a) raw powder | (b) 800°C | (c) 900°C | (d) 1000°C |
|---------|----------------|-----------|-----------|------------|
| Ca      | 93.00 ± 0.21   | 90.27 ± 0.17 | 90.24 ± 0.16 | 92.27 ± 0.17 |
| P       | 4.07 ± 0.10    | 6.07 ± 0.12 | 6.06 ± 0.12 | 4.85 ± 0.11 |
| others  | 2.93           | 3.66       | 3.7        | 2.88       |

In accordance with the EDS results, table 1 showed that calcium is a key element in the mangrove crab shells from Merauke. The percentage content of calcium were comparable fr each samples, confirmed that the calcination of crab shells with various temperature does not effected on the calcium content.
4. Conclusions

The Merauke mangrove crab shell has been characterized; despite of its low composition of protein, still it shows high calcium content. The results show that the shell powder could survive through the calcinations process at temperature of 1000 °C. In other words, it was close to bio-ceramic production that based on egg shell. The result shows that the shell of Merauke Mangrove Crab has potential application for bio-ceramic. However, further study to find the optimum synthesis method is still needed in the future.

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