Utilization of wasted cockle shell as a natural coagulant and a neutralizer of polluted water in Bangka Belitung islands, Indonesia

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Utilization of wasted cockle shell as a natural coagulant and a neutralizer of polluted water in Bangka Belitung islands, Indonesia

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Abstract. Bangka Belitung Islands is the largest tin producer in Indonesia. The high activity of tin mining caused the environmental damage which had an impact on the emergence of clean water crisis in some areas in this province. In this paper, a simple water quality improvement method based on wasted cockle shell was developed. Based on x-ray diffraction analysis it is known that calcination of cockle shell powder at 700°C will decompose the powder into calcium oxide compound. The addition of calcined cockle shell powder into acidic water from Merawang Sub-district will increase the pH of water through the process of forming hydroxide groups in the water. The calcined cockle shell powder can also coagulate pollutants in some polluted water from Koba Sub-district. The coagulation results were analyzed using SEM/EDS.

1. Introduction
Bangka Belitung Islands has been widely recognized as one of the largest tin producing regions in Indonesia even in the world [1, 2]. Tin has become a major commodity and has become a major contributor of the economy in the province, although in recent years tin mining production has declined. For example, in the year before 2010, tin production in Kepuuan Bangka Belitung reached 51,596 tons/year but in 2014 the production only reached 19,719 tons. But the problem is, often the rise of tin mining activities is not followed by good waste processing, especially by unconventional miners, causing severe environmental damage in the province [3, 4].

One of the impacts of environmental damage in the Bangka Belitung Islands is that many areas in the province have a water crisis. Many sources of water in the area of Bangka Belitung Islands are acidic and turbid. One of the areas whose water is acidic is in Merawang Sub-district, Bangka Regency. While one of the areas that whose turbid water is located in Koba Sub-district, South Bangka Regency. In our preliminary study it was found that the pH of water in some areas in Merawang Sub-district reached 5.7. The appearance of turbid water in Kecamatan Koba as shown in Figure 1. Based on the characteristics of water that is so can be concluded that the two water from this area has not satisfy the water-requirement that has been determined by the government in accordance with the decision of Ministry of Health No.907/Menkes/SK/VII/2002. It is feared that inappropriate use of such water in the long time can lead to the emergence of unexpected diseases.

Besides of tin, other potential natural resources in the Bangka Belitung Islands lies in the maritime sector. Cockle is one of the most abundant maritime potentials in the province because it can be easily found in almost all coastal areas. For example, in Selan Village, Central Bangka Regency, produce 4
tons of cockle (Andara granosa) per day and then in Kundi Village and Belo Laut Village, West Bangka Regency can produce 150 tons/year of cockle and in Pulau Lepar Pongok, South Bangka Regency, can produce snails up to 500 kg/day [5]. So, according to the value it is necessary to develop a method to utilize the wasted cockle shell. This is because about 60% - 70% of cockle's weight is its shell.

![Polluted Water](image1.png) ![Clear Water](image2.png)

**Figure 1.** In this case simply justify the caption so that it is as the same width as the graphic.

Calcium mineral in aragonite phase is the main content of a cockle shell [6]. Through calcination process, aragonite will decompose into calcium oxide. Calcium oxide is a compound which can be utilized as a pH enhancer because it can form hydroxide groups in water. So its use in acidic water is expected to neutralize pH of the water. In addition, in the presence of Ca2+ ions, cockle shell powder can coagulate pollutants in water [7]. The superiority of cockle shell powder as coagulant are its non-toxic, biodegradable, and can interact with various types of pollutants, both organic and inorganic [8]. Thus the use of cockle shell powder as a coagulant has an environment-friendly properties and can behave as a biosorbent [9].

2. Methods
Firstly, the wasted cockle shells which obtained from the seller of cockle and clams, it washed and dried in the sun to dry for 2 days. After drying the waste shells were smoothed and calcined at 700°C with variations of heating time of 2, 3, and 5 hours. Calcined cockle shell powders were then tested on acidic water from Merawang Sub-district and turbid water from Koba Sub-district. The phase of the shell powders was identified using XRD while the microstructure and the content of the coagulation product were observed by using SEM/EDS.

3. Results and Discussion
The results of the x-ray diffraction analysis of cockle shell powders before and after calcination are shown in figure 1. Based on these results it is known that, before calcination, the cockle shell contain only the CaCO3 phase in the aragonite structure. Calcination at 700°C for 3 hours causes the CaCO3 compound transform into calcite and some of CaCO3 begins to decompose into calcium oxide. Aragonite phase changes to calcite due to heat treatment have also been observed by [10]. The emergence of calcium oxide phases is indicated by the presence of calcium hydroxide compounds due to the powders contaminated with moisture from the environment. The occurrence of reactions between calcium oxide compounds with water vapor from the environment because calcium oxide is a highly reactive compound to the presence of water vapor. At the calcination for 5 hours the entire CaCO3 compound has been decomposed into calcium oxide. In the powders there is a reaction between calcium oxide with water vapor to form calcium hydroxide.
Figure 2. XRD diffraction pattern of cockle shell: before and after calcination

Graph of increase of acid water's pH from Merawang Sub-district due to the addition of cockle shell powder is shown in Figure 3. Through the results it is known that the most significant increase of pH occurs in the addition of shell powder with 5 hours calcination. In order to comply with water-use regulations, for 20 liters of acidic water Merawang Sub-district (initial pH 5.7) should be added about 0.1 to 0.25 grams of cockle shell powder with calcination for 5 hours. This significant increase in calcium oxide occurs because in the shell powder with 5 hours of heating there is a lot of calcium oxide that is reactive with water to form calcium hydroxide compounds. The presence of calcium hydroxide compounds in water will increase the hydroxide group as an indication of increased pH. The second highest increase in pH graph occurs when the addition of cockle shell powders without heating. The powders without heating process can provide a higher increase effect than powders with 3 hours calcination because the powders are floating and it difficult to solve with water. So because the pH measurement is done just on the surface of the water it is as if its pH increase is significant. This can be proven when we partially dispose of the water that has been mixed with the powders of the water (surface) its pH dropped dramatically again. This is understandable because calcium carbonate has a much lower solubility than calcium hydroxide.

Figure 3. Enhanced water pH curve due to the addition of cockle shell powder
Figure 4 shows the coagulation results of polluted water from Koba Sub-district through the addition of cockle shell powders after 6 hours. It appears that the powders with 5 hours calcination can produce water with the highest clarity level. In sequence, it can be concluded that the longer heating process then the shell powders more able to coagulate pollutant in the water. In without calcination powder it does not provide a significant coagulation effect of the pollutant.

![Figure 4](image-url)

**Figure 4.** The effect of coagulation process in polluted water from Koba Sub-district.

Based on microstructure observation result from coagulation of water pollutant in Merawang Sub-district in Figure 5, it can be seen that in coagulant formed aragonite and calcite phase. The calcite phase is shown by microstructure in the form of cubes due to having a trigonal crystal structure while the aragonite with orthorhombic crystal structure is indicated by microstructure of needles. The formation of calcium carbonate compounds, both in the aragonite and calcite phases, is also supported by EDS results indicating that in coagulants, other than the calcium element, there is also a dominant element of carbon and oxygen. So through the results of coagulant analysis can be concluded that the main pollutants that cause water in Sub-district Koba become turbid contain carbon element. In addition to carbon, some small amounts of elements such as Na, Mg, Al, Si, Fe, and Yb are also contained in the coagulation results of cockle shell powders.

![Micrographs](image-url)

**Figure 5.** (a) sem micrograph of coagulation results, (b) eds micrograph of coagulation results.

| Element | Atomic% | Element | Atomic% |
|---------|---------|---------|---------|
| C K     | 18.44   | Si K    | 0.57    |
| O K     | 60.09   | Ca K    | 19.76   |
| Na K    | 0.19    | Fe K    | 0.07    |
| Mg K    | 0.38    | Yb L    | 0.11    |
| Al K    | 0.39    |         |         |

**Table 1.** Composition of coagulation results.
4. Conclusion
Through the heating process the cockle shell powder which is composed by calcium carbonate compounds in the aragonite phase will transform into calcite phase and then decomposed into calcium oxide. The use of calcined cockle shell powder for 5 hours calcination in acidic water from Merawang Sub-district can effectively increase pH of the water through the formation of hydroxide groups. Similarly, the effectiveness of coagulation, the longer process of calcination then it more effective to be able to coagulate pollutants in water. Based on the analysis of coagulation results using SEM/EDS it known that the pollutants in the water in Koba Sub-district contain carbon that makes the calcium element to form calcium carbonate compounds.

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