Quality improvement of water from post Tin mining based on a wasted cockle shell

Y Tiandho

Department of Physics, Universitas Bangka Belitung, Jl. Kampus Peradaban, Bangka 33172, Indonesia

Corresponding author: yuant@ubb.ac.id

Abstract. The high Tin mining activity in the Bangka Belitung Islands caused a considerable amount of environmental damage in the province. One of the most common impacts of contamination is the poor quality of water. Kulong is a former excavation of Tin mines that may be used as a reservoir of water. But most kulong, especially young ones, store acidic water and dispersed-pollutant water so that it does not meet the minimum requirements of good water. In this study, we developed a simple method to improve the quality of water from post Tin mining using wasted cockle shell. The utilisation of wasted cockle shell because of its abundant amount in this province. Based on the results it is known that calcined cockle shell powder is sufficient to increase the pH level of the water and can coagulate the pollutants that contained in it. Through the water clarity level and the number of total dissolved particles in the water after testing, it is known that the cockle shell powders have a significant effect on improving quality water.

Keywords: water treatment, cockle shell, green mining.

1. Introduction
The Bangka Belitung Islands are the largest Tin-producing province in Indonesia and are among the top three Tin producers in the world [1,2]. The Tin mining sector remains the primary commodity in the region even though in recent years there has been a decline in production [3]. High Tin mining activities in the province cause severe environmental damage. The lack of wastewater treatment in the Tin mining process, especially by unconventional miners, has created a lot of water sources in this province that is polluted and does not meet the Ministry of Health Decree No.907/Menkes/SK/VII/2002 on water quality requirements [4,5]. One of the effects of poor water quality in the Bangka Belitung Islands, regardless of the daily needs of the community, is the lack of water supply to meet agriculture and freshwater fisheries needs while the freshwater aquaculture development program is one of the flagship programs for this province.

When land has undergone excessive exploration, it will produce basins, which are then called kulong. Kulong can be a source of water in the dry season, or it can be used for agricultural and fisheries purposes. However, as ex-mining land, it is feared that there are remnants of heavy metals that make kulong water unsuitable to meet these needs. One indication of the presence of heavy metals in water is its turbidity of colour and its acidity. Therefore, to be applied in agriculture and freshwater fisheries, this water requires further treatment.

The maritime sector is another potential natural resource from the Bangka Belitung Islands. One of them is cockle. The cockles can be easily found in the province’s almost all coastal areas. The primary composition of cockle shell is calcium carbonate, which is usually present in the aragonite phase [6]. The calcination process can decompose calcium carbonate into coagulated calcium oxide...
Figure 1. XRD diffraction pattern of cockle shell after calcinations

and can increase its pH to form hydroxide group in water. This hydroxide group can be created because calcium oxide powder, when encountered with acidic water, which has \( \text{H}^+ \) ions, will form calcium hydroxide [7]. Moreover, the shell powder if interacting with \( \text{Ca}^{2+} \) ions, it can coagulate the pollutants dispersed in water [7,8]. The superiority of shell powder as a coagulator is that it is non-toxic, readily biodegradable and easily interacts with other organic substances such as proteins. Even shell powder can be more effective than alum. Thus the use of shell powder as a coagulator is environmentally friendly [9]. Coagulation of pollutants in post Tin mining water is the first step in filtering heavy metals because heavy metals in water will be coagulated into larger particles so that they can be separated further.

2. Methods
Prior to use, the cockle shell waste is rinsed then dried under the sun for two days. After the drying process, cockle shell waste is then made into powder through a milling process followed by a calcination process at a temperature of 700 °C for 5, 7, and 9 hours. The phase of shell powder was identified using X-Ray Diffraction (XRD, Rigaku Smartlab 3 KV, Cu - \( \text{K}_\alpha = 1.5406 \) Å) method. XRD pattern analysis is performed using X'pert HighScore Plus software. Calcined cockle shell powder is then mixed into turbid and acidic water from the post Tin mine. The post Tin mining water used comes from Tanjungratu area in Bangka Regency. The effectiveness of water quality improvements that will be observed in this research include the aspect of turbidity, total of dissolved particles, and increased in pH. These three aspects are the basic parameters in determining water quality. The measurement of the total dissolved particles in the water is carried out using a TDS meter (TDS Testers-139) that has been calibrated with a calibration solution (1382 ppm, 25°C). The turbidity of the water is measured by a calibrated turbidimeter (HACH-2100N) using standard liquids of <0.1, 20, 200, 1000, and 4000 NTU. SEM/EDX (Hitachi, SU-3500) is used to observe the microstructure of the results of coagulation and its elements. Meanwhile, to find out the presence of heavy metal elements in water is done by atomic absorption spectroscopy (AAS) for aluminium and iron elements in water.

3. Results and discussion
The results of X-Ray Diffraction pattern from cockle shell powder after undergoing the calcination process are shown in figure 1. From these patterns, it can be concluded that calcination process effectively decomposes \( \text{CaCO}_3 \) (calcite, Ref. Code: 01-081-2027) to \( \text{CaO} \) (Ref. Code: 00-037-1497). \( \text{CaCO}_3 \) compounds remaining when the calcination carried out for 5 hours, while the other calcination
Table 1. EDX analysis of coagulated pollutants

| Elements | Weight (%) | Atomic (%) |
|----------|------------|------------|
| C        | 13.80      | 20.03      |
| O        | 62.13      | 67.72      |
| Al       | 4.73       | 3.06       |
| Si       | 4.28       | 2.66       |
| Ca       | 14.89      | 6.48       |

Figure 2. The coagulation result (red circle) with the addition of the cockle shell: (a) without calcination, (b) 5 hours calcination, (c) 7 hours calcination, and (d) 9 hours calcination.

Figure 3. (a) coagulated pollutants micrographs and (b) EDX analysis results (spectrum)

treatments, when the calcination carried out for 5 hours, while the other calcination treatments, which is 7 hours and 9 hours, CaCO₃ compound completely degradable. The presence of CaCO₃ for 5 hours calcination time shows that the calcination process is too short. The diffraction patterns also reveal the presence of Ca(OH)₂ compound (Ref. Code: 00-044-1481) after calcination process. This compound is obtained because CaO is highly reactive to moisture to form Ca(OH)₂.

After passing the mixing process of the calcined cockle shell powder into the ex-mining water and the mixture is aging overnight until the coagulation is obtained as shown in figure 2. These results indicate that the pollutants coagulation at the bottom of the container occurs because of calcined cockle shell powder. The figure also shows the effectiveness of the coagulation of pollutants with the calcination process. Without the calcination process, pollutants in water are still scattered and only partially coagulate. The calcination process converts the phase of the cockle shell powder which initially takes the form of CaCO₃ to CaO. CaCO₃ compounds are not reactive compounds in water so that their presence in water is less able to coagulate dispersed pollutants. Unlike CaO which is a
**Table 2.** Turbidity measurement of water

| Type of the cockle shell powder or water | Turbidity (NTU) |
|-----------------------------------------|-----------------|
| Post tin mining water (raw)             | 1806            |
| Without calcination                     | 147             |
| 5 hours calcination                     | 9.60            |
| 7 hours calcination                     | 3.98            |
| 9 hours calcination                     | 0.421           |

**Table 3.** Effect of the addition cockle shell powder on the number of dissolved particles in the water from post Tin mining

| Type of the cockle shell powder or water | Total dissolved particles (ppm) |
|-----------------------------------------|---------------------------------|
| Post Tin mining water (raw)             | 87                              |
| Without calcination                     | 118                             |
| 5 hours calcination                     | 122                             |
| 7 hours calcination                     | 125                             |
| 9 hours calcination                     | 121                             |

**Table 4.** The results of spectrophotometric analysis of post Tin mining water before and after the addition of cockle shell powder.

| Elements | Before treatment (mg/l) | After treatment (mg/l) |
|----------|-------------------------|------------------------|
| Al       | 0.41                    | 0.09                   |
| Fe       | 0.95                    | 0.27                   |

**Figure 4.** Results of water treatment after the separation between water and coagulation results of (a) post Tin mining water (raw), addition of cockle shell powder (b) without calcination, (c) calcination 5 hours, (d) 7 hours, and (e) 9 hours.

reactive compound in water which produces Ca²⁺ ions which bind pollutants in water, this compound also has good solubility in water and can form calcium hydroxide compounds in water. Microscopy of pollutant coagulation is shown in figure 3. The results of SEM micrographs showed that the results of coagulation had a microstructure in the form of coagulum. This coagulum is formed due to the binding of pollutant elements by Ca²⁺ ions. While the results of EDX analysis of the obtained coagulation show the presence of dominant elements of pollutants such as C, Fe, Al, and Si with details as shown in table 1. These results indicate that calcined cockle shell can bind various heavy metal elements like Fe and Al and organic elements like C.
Comparison of the appearance of water after going through the coagulant separation process is shown in figure 4. The quantitative results of water turbidity using turbidimeters are presented in table 2. Based on water turbidity after the separation from coagulant, it was found that 9 hours calcined cockle shell powder produced the highest turbidity compared to the other two. This result is also supported by the smallest water turbidity value of 0.421 NTU. Also, it can be said that the use of calcined cockle shell powders effectively reduces the turbidity of the post Tin mining water and the longer the calcination process will be more effective in coagulating pollutants in the post Tin mining water. The TDS measurement results used to analyse the number of dissolved particles in water are presented in table 3. The table shows that the highest number of dissolved particles was found for cockle shell powder calcined for 7 hours. However, in general, the calcination process of cockle shell powder increases the number of dissolved particles. This can be understood because of the dominance of high solubility CaO in water.

The atomic absorption spectrophotometric (AAS) results for water before and after mixing with cockle shell powder (9 hours of calcination) are shown in table 4. The table shows that before mixing with cockle shell powder, the water contains Al and Fe in sufficiently high amounts, and the amount is above the limit set by the Indonesian Ministry of Health. However, after being mixed with cockle shell powder, the content of Al and Fe in post Tin mining water is reduced, and the amounts meet the requirements set by the Indonesian Ministry of Health. This result corresponds to the results of EDX measurements, which obtain Al and Fe metal elements in the results of coagulation.

The pH measurement results showed an increase for post Tin mining water after being mixed with calcined cockle shell powder as shown in table 5. The table shows that the addition of cockle shell powder (mass of the shell powders: 0.05 gram and the volume of water: 240 mL) has a very significant effect in changing pH. However, it was the calcination for 7 hours that gave an increase in pH, which was close to the water conditions suitable for use. Overall, the increase in pH indicates a value above the water level that can be used, so that additional processes are still needed to filter dissolved cockle shell powder.

4. Conclusions
Based on the results obtained it can be concluded that the calcination process at temperatures of 700 °C for 7 and 9 hours can decompose CaCO₃ as a whole from cockle shell powder to CaO. The presence of Ca(OH)₂ in calcined cockle shell powder is caused by water vapour contamination from the environment. After the process of separation of water with pollutant coagulants, it can be concluded that the use of calcined cockle shell powder can significantly reduce turbidity, reduce of Al and Fe metals, and organic C elements, increase the number of dissolved particles and pH values from post Tin mining water substantially.

Acknowledgements
This research was funded by Universitas Bangka Belitung through PDTJ UBB 2017 funding scheme.

Table 5. Effect of the addition cockle shell powder on pH level of water from post Tin mining

| Type of the cockle shell powder | pH level |
|--------------------------------|----------|
| Without calcination            | 8.4      |
| 5 hours calcination            | 10.2     |
| 7 hours calcination            | 9.0      |
| 9 hours calcination            | 11.0     |

References
[1] Ibrahim 2016 GSTF Journal of Law and Social Sciences 5, 1–7
[2] Rohendi R and Aryanto N C D 2012 Bulletin of the Marine Geology 27 7–18
[3] Aspinall C 2001 Mining, Minerals, and Sustainable Development Report No. 79 pp. 1–30 (London: International Institute for Environmental Development)
[4] Syarbaini, Warsona A and Iskandar D 2014 Atom Indonesia 40 27–32
[5] Sari S P and Rosalina D 2016 Procedia Environ. Sci. 33 436–42
[6] Mohamed M, Yusup S and Maitra S 2012 Journal of Engineering Scince and Technology 7 1-10, 2012
[7] Tiandho Y, Aldila H, Mustari, Megiyo and Afriani F 2018 J. Phys.: Conf. Ser. 1013 012181
[8] Moideen S N F, Din M F M, Ponraj M, Yusof M B M, Ismail Z, Songip A R and Chelliapan S 2015 Desalin. Water Treat. 571–9
[9] Daud Z, Abubakar M H, Kadir A A, Latiff A A A, Awang H, Halim A A and Marto A 2017 International Journal of Geomate 12 46–52