Efficiency of sea shells and crab shells waste as eco-friendly adsorbent for treating acid rock drainage

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Abstract. Acid rock drainage is a major environmental problem but also many of the availability of a vast array of remediation techniques and technologies. The current study aims to apply crushed sea shells and crab shell as an efficient and cost effective adsorption medium for acid rock drainage treatment in batch studies. The effects of adsorbent mass and solution pH were investigated in batch studies whilst initial concentration. The preliminary results showed that sea shell and crab shell derived adsorbent has a great potential as an alternative material in the treatment of acid rock drainage compared to limestone.

1. Introduction

Acid rock drainage is a major environmental issue by mining operations. It is formed from the exposure of Potential Acid Forming (PAF) material to water and oxygen. Acid rock drainage generally is characterized by low pH and high heavy metal toxicity. Wastewaters containing heavy metals and low pH must be treated before being discharged into water bodies. Various passive and active methods are used to neutralize acidity and reduce levels of heavy metals.

Acid rock drainage treatment typically involve alkali material addition in order to raise the pH. Limestone (CaCO₃) one of calcareous materials is the most widely applied to treat acid rock drainage, due to low cost, available in large quantities, and simplicity of treatment plant [1]. The presence of abundant sea shells and crab shells were generate domestic waste, in this study sea shells and crab shells was used as an alternative adsorbent for treaing acid rock drainage. Bioadsorbent (sea shells and crab shells) adsorption possesses particular strengths because there are eco-friendly benign, abundant and cost effective.

Several research have been developed over the years for treating acid rock drainage, such as natural limestone [2] and eggshell [3,4]; chitosan nanoparticles and crab shells [5]; also sea shells for for the treatment of water contaminated with acid rock drainage [6]. Thus the aim of this research was to examine sea shell and crab shell as a eco-friendly adsorbent for treating acid rock drainage. Therefore, the purpose of this study was to evaluate the efficiency of the use of shell and crab shells compared to the use of natural limestone, to neutralize acid mine water.
2. Material and Methods

2.1. Acid Rock Drainage Water Sample
The acid mine water was sampled from the gold ore mining area in Selogiri, Wonogiri, Central Java Province. The water sample is placed on a 5 liter high density polyethylene (HDPE) container and sealed with an airtight cap. The water samples are then taken to the laboratory for analysis. Acid rock drainage is highly acidic pH=3.83; which was far below the recommended values (6-9) by the Minister of Environment Decree No. 202 Year 2004 Regarding Waste Water Standard for Gold and Copper Mine Activities and/or Bussinesses [7].

2.2. Adsorbent Preparation
Sea shells and crab shells waste were collected from restaurant near Depok Beach, Bantul, Yogyakarta. The shells were washed with water to remove sand and other impurities. The shells were dried. Then, the dried shells were crushed and sieved into particle size of 200 mesh. Natural limestone were drawn from the local limestone plant in Karangasem, Ponjong, Gunungkidul, Yogyakarta. Limestone crushed with a particle size of 200 mesh (Figure 1).

![Figure 1. Process of Acid Rock Drainage Treatment](image)

2.3. Batch Adsorption
Batch experiment were conducted to investigate the treatment efficiency under different conditions. Adsorbent type and dosage as a variable was explored by adding 0.2; 0.4; 0.6; 0.8; and 1 g in 500 mL of acid rock drainage in order to raise the pH to between 6 and 9. The samples were placed in the plastic bottle and then the samples were manually stirred. Over the batch experiment duration, three periods have been explored of treated acid rock drainage: 1 h; 24 h; and 48 h. The pH raise efficiency was calculated as follows [4]:

\[
    R = \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \tag{1}
\]

where \(C_i\) and \(C_f\) are initial and final concentrations (mg/L) in the raw and treated acid rock drainage.
3. Result
The efficiency of dose and type of adsorbent depends on the rate of neutralization reaction and selected indicator (the target pH value selected as pH 6-9). The solid-liquid ratio is one of important variable of efficiency for treating acid rock drainage. The neutralization with alkaline material was observed by monitoring changes in pH values of acid mine water within 1 h; 24 h; and 48 h. The increase of pH value at the determined time was respect to the optimal dose. Then the efficiency of dose and type of adsorbent taken into an option possible substitution of natural limestone by eco-friendly alkaline material such as sea shells and crab shells powder.

3.1. Neutralization using different alkaline material
This stage was to identify an optimal dose of sea shells powder to reach the pH value at around 6 to 9. A significant increase pH occurs in one hour after dosing the powder. Table 1 shows pH value after treatment with sea shells powder. The exposure of the sea shells powder to acid mine water for an hour showed an increase pH value with optimal dose was 1 g. Then the exposure of powder after 24 h showed an increase pH value with optimal dose was 1 g. Whilst the acid mine water treatment for 48 h showed the optimal dose was 6 g. Further growth was rather slow after 48 h the pH value was 8,20; 8,30; 8,34; 8,33; and 8,30 respectively for the doses below (Table 1). The applied doses of crab shells powder were sufficient to reach the pH value of around 6 to 0. Significant increase in the pH value from 3,83 to 8,67 at doses of 1 g crab shells powder occur during 48 h. The result from treatment by added natural limestone that required pH value around 6 to 9 was obtained in case of optimal dose 0,2 g.

| Table 1. pH value after treatment with different alkaline material. |
|---|
| **Alkaline Material** | **Dose (g)** | **After Treatment (hour)** |
|   |   | **0** | **1** | **24** | **48** |
| **Initial** | - | 3.83 | 3.83 | 3.83 | 3.83 |
| **Sea shells** | 0.2 | 3.83 | 6.59 | 8.09 | 8.20 |
|   | 0.4 | 3.83 | 7.09 | 8.14 | 8.30 |
|   | 0.6 | 3.83 | 7.18 | 8.16 | 8.34 |
|   | 0.8 | 3.83 | 7.25 | 8.16 | 8.33 |
|   | 1 | 3.83 | 7.34 | 8.17 | 8.30 |
| **Crab shells** | 0.2 | 3.83 | 6.88 | 8.37 | 8.38 |
|   | 0.4 | 3.83 | 7.05 | 8.43 | 8.47 |
|   | 0.6 | 3.83 | 7.52 | 8.53 | 8.59 |
|   | 0.8 | 3.83 | 7.65 | 8.57 | 8.64 |
|   | 1 | 3.83 | 8.05 | 8.60 | 8.67 |
| **Natural limestone** | 0.2 | 3.83 | 6.85 | 8.11 | 8.29 |
|   | 0.4 | 3.83 | 6.94 | 8.12 | 8.25 |
|   | 0.6 | 3.83 | 6.99 | 8.13 | 8.24 |
|   | 0.8 | 3.83 | 7.02 | 8.09 | 8.23 |
|   | 1 | 3.83 | 7.09 | 8.03 | 8.22 |
3.2. Efficiency of the different alkaline material
The dose of different alkaline material is one of factor that affect the efficiency of increase pH value. The efficiency of different alkaline material on the acid mine water treatment is shown in Table 2, respectively. Result shows that crab shells was the highest efficient as an eco-friendly alkaline material substitution of natural limestone.

The effect of sea shells and crab shells dose (0.2; 0.4; 0.6; 0.8; and 1 g) on the efficiency investigated, owing to their positive preliminary results. After the equilibration the final pH of each treated acid rock drainage water sample was measured and recorded. Finally, the effect of contact time on increase the pH value was explored by adding 0.6 g of sea shells; 1 g of crab shells, and 0.2 g of limestone powder into 500 mL of raw water sample.

The highest efficiency for treating acid rock drainage by using crab shells. Exposure crab shells at 500 mL acid water sample shows that efficiency increased with increase in crab shells dose. Specifically, at a fixed crab shells dose of 1 g, the efficiency of pH value increase up to 55.82% for 48 hr treatment.

Moreover, sea shells which could also have played an important role in the neutralisation process. Sea shells efficiency value is 54.08% by adding 0.6 g after 48 hr treatment. This efficiency value is higher than the efficiency value of natural limestone.

As a result, acid neutralisation increase and the overall treatment efficiency improves. The pH value by adding sea shells and crab shells showed similar trend, whereby the pH value of treated water increased slightly, followed by dose adding.

| Alkaline Material | Dose (g) | Efficiency (%) at time of treatment (hour) | 1 | 24 | 48 |
|-------------------|----------|--------------------------------------------|----|----|----|
|                   |          |                                            |    |    |    |
| Initial           | -        |                                            | -  | -  | -  |
| Sea shells        | 0.2      | 41.88                                      | 52.66 | 53.29 |
|                   | 0.4      | 45.98                                      | 52.95 | 53.86 |
|                   | 0.6      | 46.66                                      | 53.06 | 54.08 |
|                   | 0.8      | 47.17                                      | 53.06 | 54.02 |
|                   | 1        | 47.82                                      | 53.12 | 53.86 |
| Crab shells       | 0.2      | 44.33                                      | 54.24 | 54.30 |
|                   | 0.4      | 45.67                                      | 54.57 | 54.78 |
|                   | 0.6      | 49.07                                      | 55.10 | 55.41 |
|                   | 0.8      | 49.93                                      | 55.31 | 55.67 |
|                   | 1        | 52.42                                      | 55.47 | 55.82 |
| Natural limestone | 0.2      | 44.09                                      | 52.77 | 53.80 |
|                   | 0.4      | 44.81                                      | 52.83 | 53.58 |
|                   | 0.6      | 45.21                                      | 52.89 | 53.52 |
|                   | 0.8      | 45.44                                      | 52.66 | 53.46 |
|                   | 1        | 45.98                                      | 52.30 | 53.41 |
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