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Efficacy of Limestone and Laterite Mine Waste in the Passive Treatment of Acid Mine Drainage

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Acid mine drainage (AMD) treatment is continuously being researched due to its detrimental effects to the surrounding ecosystem and nearby communities. Although active treatment is the most widely used approach, the system needs constant input which does not make it viable in the long term. Since AMD persists long after abandonment of mine operations, passive treatment system may provide the long-term solution that can be made sustainable using materials that are cheap and derived from waste. Laterite mine waste (LMW) has shown its potential as an effective treatment media for heavy metals in AMD. In this study, the efficacy of this material to complement the performance of limestone was examined at four different ratios. The materials were placed in a layered setup to allow each material to be independent of the breakthrough point of the other. Water quality parameters (pH and conductivity) were measured along with Cu, Fe, and Ni. The results showed that a longer residence time and an increasing amount of LMW yielded better effluent quality in general. At the 30-min mark, the 25:75 (w/w) ratio of limestone and LMW increased pH from 2.24 to 5.84 while achieving a 99 % reduction for Cu, 93 % for Fe, and 63 % for Ni.

1. Introduction

Acid mine drainage (AMD), also called acid rock drainage (ARD) is a severe pollutant that is caused mainly by mine sites and activities (Moodley et al., 2018). Acid mine drainage is caused by a series of processes and chemical reactions involving the geochemistry of mineral deposits, oxygen, water, microorganisms, and temperature, and is heavily reliant on the environment in which it is generated (Lopez et al., 2018). Passive treatment systems of AMD attend to the contaminated water immediately as it passes through the system and does not require a constant state of being manned or managed by people. These systems rely on natural biological and geochemical processes (Zipper et al., 2011). Passive treatment systems are viewed as a method that is better economically because they do not need continuous chemical inputs like in active treatment systems (Kefeni et al., 2017). Passive treatment techniques typically use limestone ($CaCO_3$), according to Park et al. (2019), with anoxic limestone drains (ALDs) being used to treat acidic waters. However, ALDs are not capable of treating all AMD waters; significant concentrations of oxygen gas, aluminum, or iron (III) will cause an ALD to clog with metal hydroxide when a pH of 4.5 or above is reached (Skousen et al., 2017).

Some studies look at alternative materials, with a focus on waste such as phosphate carbonated wastes (Ouakibi et al., 2014), waste mussel shells (Crombie et al., 2011), fly ash (Ríos et al., 2008), and laterite mine waste (LMW) (Turingan et al., 2020), that may address the shortcomings seen in ALDs. A combination of materials (Muhammad et al., 2015) have shown to produce better effluent quality compared to individual materials. The availability of these materials and their efficiency in treating local AMD may significantly vary. A previous study (Turingan et al., 2020) determined the potential of LMW, a locally-abundant material, for AMD

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treatment to be due to goethite (α-FeOOH). Goethite is a naturally occurring iron oxy-hydroxide typically formed under oxidizing conditions as a weathering product of iron-bearing minerals (Mohapatra et al., 2008). When LMW was layered with limestone, the system achieved a higher metal removal than limestone and a higher pH than LMW.

The main objective of this study was to determine the most ideal ratio (25:75, 50:50, 75:25, 100:0 w/w) of limestone to laterite mine waste (LMW) in the passive treatment of AMD. The specific objectives of this study are determining the possible effects of different ratios of LMW and limestone as well as the effects of residence time in separate batch tests in the passive treatment of acid mine drainage in terms of physicochemical properties (pH level, conductivity, and metals (Cu, Fe, Ni) concentration).

2. Methodology

2.1 Materials and equipment

Raw samples of limestone and LMW went directly to the lab from a mining site in Mindanao without any pretreatment. The limestone samples were crushed to a diameter of 4 mm. The synthetic AMD solution was made by adding various concentrations of the following analytical grade reagents, the concentrations of which were based on an experiment by Bernier (2005). 1.5 M Sulfuric acid was used for the pH adjustment of AMD.

Table 1: Reagents in Synthetic AMD

Reagent used	Amount used per 5L synthetic AMD (g)	Theoretical metals concentration (ppm)
$FeSO_4.7H_2O$	46.76	1,879.35
$NiSO_4.6H_2O$	6.71	299.75
$Al_2(SO_4)_3.18H_2O$	12.34	99.95
$CuSO_4.5H_2O$	1.00	50.92
$MnSO_4.H_2O$	1.00	65.01
$MgSO_4.7H_2O$	1.01	19.73

Tabulated below are the equipment utilized in identifying the electrochemical properties of the synthetic solution and measuring the operating parameters of each batch test.

Table 2: Equipment used for measurement

Parameters	Equipment
pH and redox potential	ORION STAR A211 pH meter
Conductivity and total dissolved solids	ORION STAR A212 conductivity meter
Metals concentration	Atomic Absorption Spectrometry
Sulfates concentration	Turbidimetric Method

2.2 Batch test

The effect of residence time of limestone and LMW in the synthetic AMD was determined through two (2) trials of batch test with 6 sampling times up to 30 min. Limestone accounted for the lower layer of the batch reactor and was topped off with LMW, making the total media mass 4,400 g. A total of 2,400 mL of synthetic AMD was added to accomplish the 0.5454 (mL/g) ratio of synthetic AMD and total amount of treatment media

Table 3: Limestone to laterite mine waste ratio

Limestone (g)	Laterite mine waste (g)	Ratio (w/w)
1,100	3,300	25:75
2,200	2,200	50:50
3,300	1,100	75:25
4,400	0	100:0

Fifty (50) mL of treated AMD was drained from the batch reactor at specific sampling times (1, 3, 5, 10, 15 and 30 min) to measure pH, redox potential, and TDS. Regular filter paper was used to filter the 50 mL samples before being stored in the refrigerator. Samples for the first trial and the raw AMD were subjected to syringe filtration and dilution in preparation for atomic absorption spectrometry to showcase preliminary results. The concentration of Fe and Cu present in each sample were analyzed and recorded.

3. Results and discussion

3.1 Effect on the physicochemical properties

Figure 1 shows that the immediate increase in pH among all ratios were similar reaching a pH value of 4 to 5 from the initial 2.24 pH value of the synthetic AMD. The pure limestone setup has the largest increase at the 1-min interval but falls behind the other ratios with laterite mine waste (LMW) over time. From the 3-min to the 30-min interval, the ratios with LMW had a gradual increase in pH with the 25:75 (w/w) ratio having the biggest difference from its pH at 1 min. After 30 min each ratio reached their highest effluent pH, the pure limestone ended up with the lowest effluent pH at 5.09 while the 25:75 ratio (w/w), containing the largest amount of LMW among the four ratios, achieved the highest effluent pH at 5.84.

The higher pH value exhibited by 100:0 (w/w) ratio may have been caused by efflorescence on the surface of limestone. This is evident with the decrease seen from the 1-min to the 5-min mark before once again increasing. Contrary to that, the pH increase of the other ratios relative to the 1-min mark show that the treatment mechanism of LMW may be more dependent on adsorption rather than neutralization due to the presence of goethite (α-FeOOH). Despite the difference in treatment, Figure 1 shows the effectiveness of LMW in increasing pH when used with limestone, achieving a synergistic effect that exceeds the performance of the individual materials (Turingan et al., 2020).

The pH increase achieved by the setup is lacking compared to other materials or a combination thereof from other studies. Waste mussel shells (Crombie et al., 2011), and magnesite (Masindi et al., 2015) reached pH levels well above pH 6 despite having a similar influent pH < 3. In the study of Rakotonimaro et al. (2016), wood chips mixed with wood ash, calcite, or dolomite was able to increase pH by 4 magnitudes, reaching values above pH 8. Considering the use of multiple treatment materials, the inadequate pH increase exhibited by the system may be remedied by mixing wood chips, or other relatively inert materials, with the limestone layer to increase surface area. Since all four ratios show no sign of reaching a peak pH value at 30 min, the treatment time may also be extended to reach a higher pH.

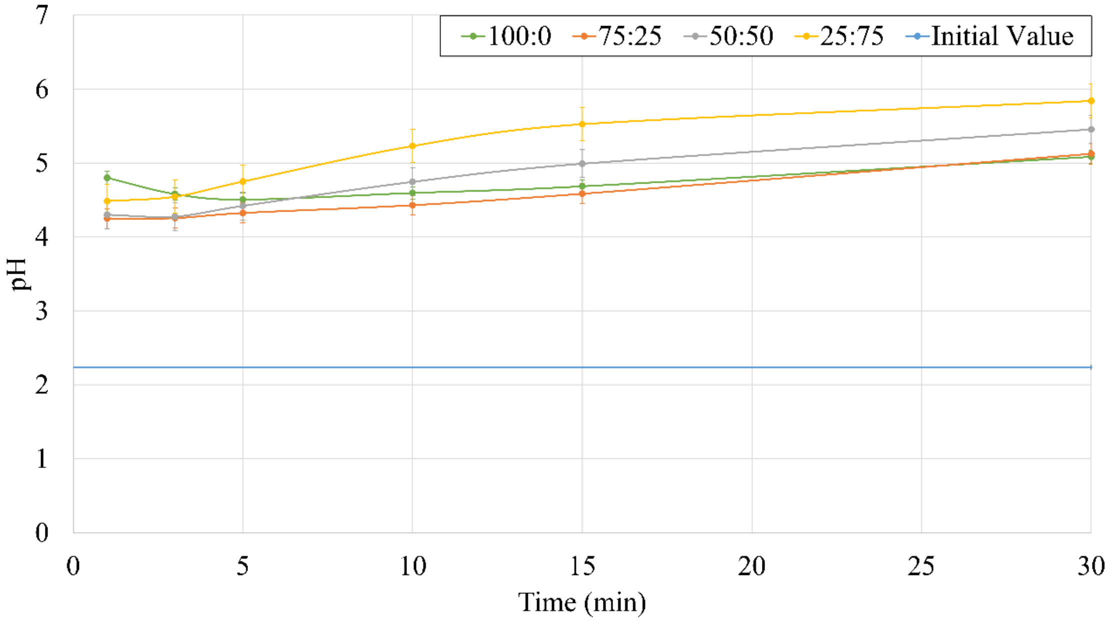


Figure 1: Change in pH over time

Conductivity is indicative of the ions present in the sample. In Figure 2, we see a relatively flat graph for the 100:0 (w/w) and 75:25 (w/w) ratio while a downward trend is seen for the 50:50 (w/w) ratio. On the other hand, the 25:75 (w/w) ratio has a significant decrease from the 1-min to the 3-min interval which continues to below 3 mS/cm by the 30-min mark. Given that none of the graphs for metal removal show the same trend as conductivity and the chemical composition of the synthetic AMD, it may be that the conductivity levels are reflective of sulfate concentration or other ions which were not part of the analysis. The drop in conductivity is also more noticeable over time as the amount of limestone decreases.

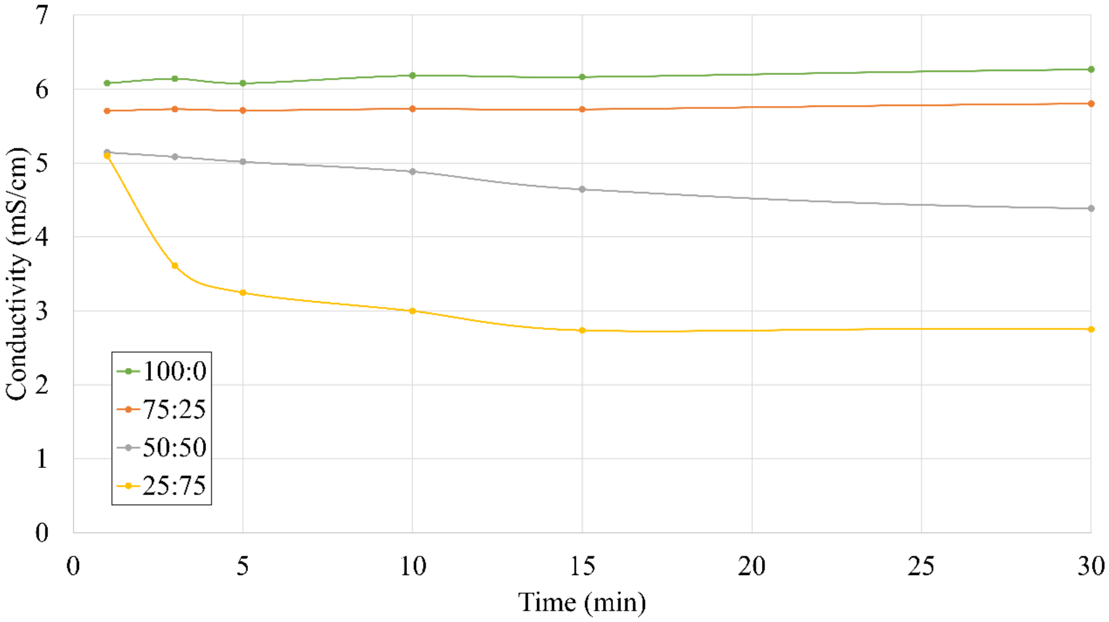


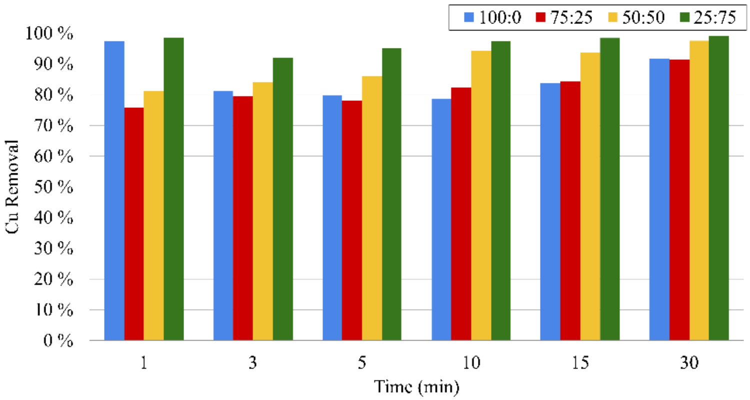
Figure 2: Change in conductivity over time

3.2 Effect on heavy metals

Figure 3 shows that the removal of Fe, Cu, and Ni is directly affected by the amount of LMW present in the setup. The 100:0 (w/w) ratio initially removes about 40 % of Fe and Ni, and 88 % Cu. On the other hand, the optimal ratio of 25:75 (w/w) reaches a maximum removal efficiency for Fe, Ni, and Cu of 91.73 %, 90.38 %, and 96.49 % respectively. However, the removal efficiency for Ni is not sustained throughout the batch test and instead settles at 63.65 % at the 30-min mark.

The pH has an observable effect on the adsorption of Cu. It is seen that, as pH increases over time, percentage removal of Cu increases similar to the observation of Ahmad et al. (2009). Generally, the results exhibited a trend showing a higher removal efficiency at a longer residence time. Furthermore, the ratio of 25:75 (w/w) limestone to LMW was proven to be most effective. This may be due to the maximum adsorption capacity of goethite to copper being found to be 37.25 mg/g (Uddin, 2017).

In the study of Muhammad et al. (2015), limestone, as the source of alkalinity, was mixed with spent mushroom compost, activated sludge, and woodchips. An overall efficiency of 88.15 % was achieved by the substrate in treating synthetic AMD containing Mn, Fe, Cu, Pb, Zn metals over 7 hours. The results are far from the 99.9 % Fe removal achieved by wood ash mixed with wood chips (Rakotonimaro et al., 2016) which was observed after 7 days in a 91-day period. Relative to the short retention time used in this study, the metal removal efficiency of the LMW-limestone system proves to be effective especially for Fe, Ni, and Cu. Considering the changes that may be implemented in the system to reach a higher pH, the metal removal efficiency may likewise increase.



(a)

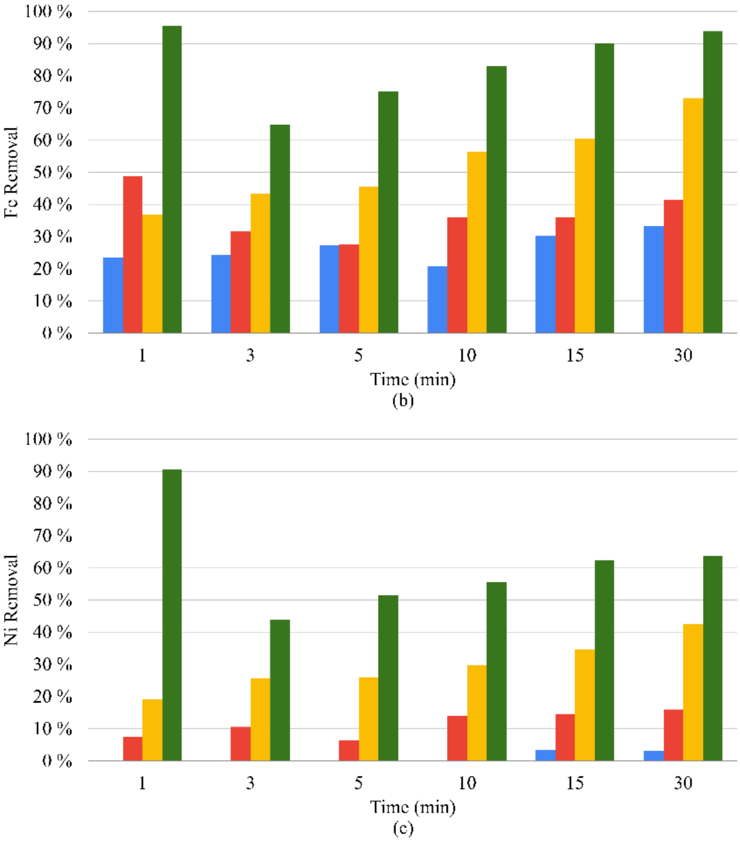


Figure 3: (a) Cu (b) Fe (c) Ni removal over time

4. Conclusions

The study used limestone and laterite mine waste (LMW) as layered multimedia for the treatment of synthetic AMD. LMW used in this study is locally-sourced and may have different characteristics compared to those found in other countries given the heterogeneity of the material unlike that of limestone. Each run was limited to 30 min in consideration of the field deployment of the system.

As the amount of LMW present in the setup increased, the change in each parameter also increased. Results show that the optimal ratio was 25:75 (w/w) with the highest efficiency observed at the 30-min mark. pH increased from 2.24 to 5.84 while conductivity stabilized at 2.548 mS/cm. At this ratio, Fe, Ni and Cu exhibited the highest sustained removal rates at 93.77 %, 63.65 %, and 99.15 %. Iron and nickel reduction increased by 24 % and 20 % compared to the setup which utilized limestone only (100:0 w/w) to treat AMD. The large amount of LMW used in the 25:75 (w/w) ratio significantly increased the heavy metal reduction which in turn allowed limestone to neutralize the AMD to a higher pH. The results show that LMW may be used as an adsorbent to complement limestone in the treatment of AMD.

Since LMW is a waste material while limestone is locally-abundant, the implementation of a treatment system composed of these materials will only incur transportation and labor costs during its setup. As a passive treatment system, operating costs will only be for the replacement of the materials in each layer once they reach their total treatment capacity. Future studies will be focused on determining the treatment capacity of each material, and the system.

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