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THE USE OF LOW GRADE LIMESTONE IN ACID MINE DRAINAGE TREATMENT

(Penggunaan Batu Kapur Bergred Rendah dalam Rawatan Saliran Lombong Berasid)

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Abstract

In this study, low grade limestone (LGL) was used in treating acid mine drainage (AMD). Based on X-ray fluorescence (XRF) result, the content of calcium carbonate mineral in limestone used was around 80% that can be considered as LGL. The pH of AMD samples increased after treated with all parameter weights of LGL at every five minutes of interval times. The parameters weights of LGL used in the experiments were 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 g. For every parameter weight of LGL, the interval times used were 0, 5, 15, 20, 25 and 30 minutes. The highest of pH value obtained was 6.44 ± 0.00 by using 6.0 g of LGL at interval time 30 minutes. The suitable pH value chosen was 6.11 ± 0.00 by using 5.0 g of LGL at interval time 20 minutes because the parameter had complied with Standards A and B of Environmental Quality Act 1974 with less cost compared to other parameters. Heavy metals content such as arsenic, cadmium, chromium, iron, manganese and zinc had decreased after reaction with all LGL weights. The content of arsenic in AMD samples after reaction with all LGL weights had complied with both standards' requirement except with 1.0 g of LGL. The percentage of removal heavy metals by using all parameter weights of LGL such as arsenic, cadmium, chromium, iron, manganese and zinc were around 98.8 to 99.8%, 53.8 to 88.5%, 94.7 to 96.5%, 99.6 to 100%, 34.6 to 38.9% and 27.0 to 90.1%, respectively.

Keywords: limestone, acid mine drainage, heavy metal

Abstrak

Dalam kajian ini, batu kapur bergred rendah (LGL) telah digunakan dalam rawatan saliran lombong berasid (AMD). Berdasarkan keputusan pendaflour sinar-X (XRF), kandungan mineral kalsium karbonat di dalam batu kapur yang digunakan adalah sekitar 80% yang boleh dianggap sebagai LGL. pH sampel AMD telah bertambah selepas bertindakbalas dengan semua parameter berat LGL pada setiap lima minit selang masa. Parameter berat LGL yang digunakan dalam eksperimen adalah 1.0, 2.0, 3.0, 4.0, 5.0 dan 6.0 g. Untuk setiap parameter berat LGL, selang masa yang digunakan adalah 0, 5, 10, 15, 20, 25 dan 30 minit. Nilai pH yang paling tinggi diperolehi adalah 6.44 ± 0.00 dengan menggunakan 6.0 g LGL pada selang masa 30 minit. Nilai pH yang paling sesuai telah dipilih adalah 6.11 ± 0.00 dengan menggunakan 5.0 g LGL pada selang masa 20 minit kerana parameter ini adalah kurang kos untuk mematuhi Piawai A dan B berbanding parameter yang lain. Kandungan logam berat seperti arsenik, kadmium, kromium, besi, mangan dan zink telah berkurangan selepas bertindakbalas dengan semua berat LGL. Kandungan arsenik dalam sampel-sampel AMD selepas bertindakbalas dengan semua berat LGL telah dipatuhi dengan kehendak kedua-dua standard kecuali dengan menggunakan 1.0 g LGL. Peratusan penyingkiran logam berat dengan menggunakan semua parameter berat LGL seperti arsenik, kadmium, besi, mangan dan zink masing-masing adalah sekitar 98.8 hingga 99.8%, 53.8 hingga 88.5%, 94.7 hingga 96.5%, 99.6 hingga 100%, 34.6 hingga 38.9% and 27.0 hingga 90.1%.

Kata kunci: batu kapur, saliran lombong berasid, logam berat

Introduction

Limestone is a versatile material that can be used in many industries such as paper making, glass, food, plastics, paint, rubber, etc. [1, 2]. Limestone is a sedimentary rock with chemical formula $CaCO_3$ [3] and 4% of the earth crust contains carbonate mineral that consists limestone, chalk and biominerals [4]. Limestone also can be used as a neutralization agent in treating acidic water especially in treating AMD [5]. Other materials that can be used to treat AMD are organic material [6], carbide lime [7], hydrated lime [8], quicklime [9], etc. In this study, low grade limestone was used in treating AMD. Limestone with the content of calcium carbonate mineral less than 94% can be classified as LGL [10]. The objective of this study is to show that LGL can be used as a material in treating AMD.

AMD is a global environmental problem caused by oxidation of sulphide minerals [11] such as pyrite, marcasite, arsenopyrite, sphalerite, chalcocite, etc. with the presence of water and sulphate oxidizing bacteria (SOB). AMD occurs can be shown in equations 1 to 3 [12].

$$FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (2)$$

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \longrightarrow 15FeSO_4 + 8H_2SO_4 \quad (3)$$

AMD can be defined as acidic water in which its pH is less than 5, contains high concentration of sulphate and heavy metals such as arsenic, copper, lead, nickel, zinc, etc.

Materials and Methods

Study area

The study is focussed on the AMD problem that occurred in a tin tailing pond. The tin tailing pond is in a tin mine located in northern Perak. The tin tailing pond is a recycled pond which involves the activities related to tin ores.

Materials

In this study, LGL was used as neutralization agent and obtained from Pengkalan Hulu, Perak. AMD sample was collected from tin tailing pond also located in Pengkalan Hulu, Perak.

Instrumentation

Elemental analyses for LGL sample were determined by X-ray fluorescence using Shimadzu XRF-1700 sequential X-ray fluorescence spectrometer. The pH were measured using a Mettler Toledo Ross FE 20 pH meter. The metal ions concentrations of the AMD samples were analysed by Perkin Elmer Optima DV 5300 ICP-OES.

Methods

Six experiments were carried out with different weights of low grade limestone used 1, 2, 3, 4, 5 and 6 g, respectively. The different weights of limestone were added into individual 1 L beakers that contained 500 mL AMD samples. The AMD samples with different limestone weights were stirred at 500 rpm by using overhead mechanical stirrer. During the stirring process, pH values of the solutions were recorded at interval times of 0, 5, 15, 20, 25 and 30 minutes. The AMD samples were analysed by using ICP-OES for heavy metals content before and after reaction. Figure 1 shows the jar test of LGL reacted with AMD and Figure 2 shows the LGL samples before and after reaction with AMD.

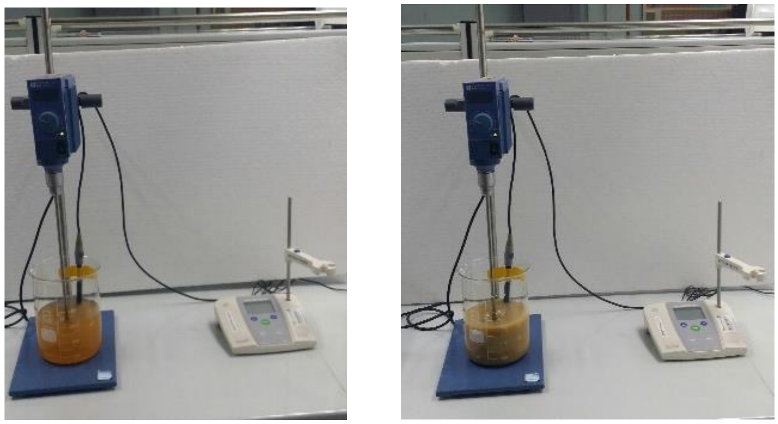

Figure 1. Jar test of AMD reacted with LGL

Figure 2. LGL before and after reaction with AMD sample

Results and Discussion

XRF result in Table 1 shows that the limestone used in this study was low grade because the content of calcium oxide obtained was 44 % as shown in Table 1. The percentage of calcium carbonate calculated was around 80% which indicates that it is a low grade limestone [3].

Table 1. X-ray fluorescent analysis result

Element Oxide	**Result (%)**
Fe_2O_3	0.48
MnO	0.11
TiO_2	0.20
CaO	44.15
K_2O	1.08
SiO_2	19.24
Al_2O_3	3.28
MgO	0.89
Na_2O	0.08

Table 2 shows the pH values of AMD samples before and after reaction with LGL as neutralisation agent. The initial pH of AMD samples was ~2.47. The highest pH obtained was 6.44 ± 0.00 by using 6.0 g of LGL at interval time 30 minutes. However, the optimal parameters selected was 5.0 g of LGL with retention time of 20 minutes which resulted in pH value of 6.11 ± 0.00. These parameters were chosen because it complied with Standards A and B of Environmental Quality Act 1974 which stated that the pH value for Standards A and B are 6.0 and 5.5 [13], respectively. Standard A refers to the discharge of effluent is upstream from catchment area and Standard B refers to the discharge of effluent is downstream from catchment area. Furthermore, the selected parameters will cost less in order to reach pH 6 compared to the other parameters. The reaction between LGL and AMD sample is shown in equation 4. pH value increase with the increasing of time caused to a lot of calcite ($CaCO_3$) dissolved in AMD sample. The reaction between LGL with AMD produced calcium ion (Ca^{2+}) and carbonic acid (HCO_3^-). Carbonic acid further reacted with hydrogen ion (H^+) to produce water and carbon dioxide gas. As a result, the use of H^+ can increase pH in AMD sample after the reaction [14].

$$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^- \qquad (4)$$

Table 2. pH of AMD sample before and after reaction with six different weights of LGL

Weight of LGL (g)	Interval Time (minutes)	pH	
		Before Reaction	After Reaction
1.0	5	2.47 ± 0.00	3.84 ± 0.00
	10	2.47 ± 0.00	4.00 ± 0.00
	15	2.47 ± 0.00	4.07 ± 0.00
	20	2.47 ± 0.01	4.12 ± 0.00
	25	2.47 ± 0.01	4.15 ± 0.00
	30	2.47 ± 0.01	4.18 ± 0.01
2.0	5	2.47 ± 0.00	4.35 ± 0.01
	10	2.47 ± 0.00	4.72 ± 0.01
	15	2.47 ± 0.00	4.98 ± 0.00
	20	2.47 ± 0.01	5.16 ± 0.00
	25	2.47 ± 0.01	5.43 ± 0.01
	30	2.47 ± 0.01	5.50 ± 0.00
3.0	5	2.47 ± 0.00	4.90 ± 0.01
	10	2.47 ± 0.00	5.27 ± 0.01
	15	2.47 ± 0.00	5.54 ± 0.00
	20	2.47 ± 0.01	5.75 ± 0.00
	25	2.47 ± 0.01	5.92 ± 0.01
	30	2.47 ± 0.01	6.04 ± 0.01
4.0	5	2.47 ± 0.00	5.09 ± 0.00
	10	2.47 ± 0.00	5.52 ± 0.01
	15	2.47 ± 0.00	5.79 ± 0.01
	20	2.47 ± 0.01	5.99 ± 0.00
	25	2.47 ± 0.01	6.13 ± 0.01
	30	2.47 ± 0.01	6.24 ± 0.01

Table 2 (cont'd). pH of AMD sample before and after reaction with six different weights of LGL

Weight of LGL (g)	**Interval Time (minutes)**	**pH**	
		Before Reaction	**After Reaction**
5.0	5	2.47 ± 0.00	5.27 ± 0.00
	10	2.47 ± 0.00	5.65 ± 0.01
	15	2.47 ± 0.00	5.92 ± 0.01
	20	2.47 ± 0.01	6.11 ± 0.00
	25	2.47 ± 0.01	6.23 ± 0.01
	30	2.47 ± 0.01	6.33 ± 0.01
6.0	5	2.47 ± 0.00	5.36 ± 0.00
	10	2.47 ± 0.00	5.75 ± 0.01
	15	2.47 ± 0.00	6.04 ± 0.01
	20	2.47 ± 0.01	6.23 ± 0.00
	25	2.47 ± 0.01	6.34 ± 0.00
	30	2.47 ± 0.01	6.44 ± 0.00

Table 3 shows the heavy metals content in AMD samples before and after reaction with LGL. The results show that the content of heavy metals in AMD samples such as arsenic, cadmium, iron, chromium, manganese and zinc decreased after treated with LGL. Iron and chromium can be effectively treated by using LGL because the result show that in all AMD samples, the percentage of iron and chromium removal were more than 95%. Their final concentrations complied with Standards A and B, iron are 1.0 mg/L and 5.0 mg/L, whereas for chromium (III) are 0.20 mg/L and 1.0 mg/L, respectively. For chromium (VI), Standards A and B is 0.05 mg/L. The concentration of arsenic obtained after reaction complied with both standards except with 1.0 g of LGL that did not reach pH value 5. The optimum of pH for arsenic removal is around 5 [15]. Standards A and B for arsenic are 0.05 mg/L and 0.10 mg/L, respectively. For zinc, its concentration complied with both standards after reaction with 4.0, 5.0 and 6.0 g of LGL, respectively. Standards A and B for zinc is 2.0 mg/L. The concentrations of manganese and cadmium obtained after reaction in all parameters did not comply with both standards because manganese and cadmium can only be precipitated at pH around 10 and 11, respectively. Other techniques such as adsorption and oxidation are suitable to be used in treating manganese and cadmium. The reaction between AMD samples and LGL produced precipitation. Precipitation is one of the separation techniques to reduce heavy metals content in AMD samples. Heavy metals such as iron or zinc can be precipitated as carbonate or hydroxide metals as shown in Equations 5 and 6, respectively [14].

$$Fe^{2+} + HCO_3^- \longrightarrow FeCO_3 + H^+ \quad (5)$$
$$Zn^{2+} + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+ \quad (6)$$

Table 3. Heavy metals content in AMD samples before and after reaction with LGL

LGL Weight (g)	**Element**	**Before Reaction (mg/L)**	**After Reaction (mg/L)**	**Percentage Removal of Heavy Metals**
1.0	As	6.44 ± 0.34	0.08 ± 0.00	98.8
	Cd	0.26 ± 0.01	0.12 ± 0.00	53.8
	Fe	317.27 ± 13.41	1.41 ± 0.02	99.6
	Cr	0.57 ± 0.02	0.03 ± 0.00	94.7
	Mn	61.63 ± 2.65	40.29 ± 0.22	34.6
	Zn	11.49 ± 0.45	8.39 ± 0.05	27.0

Table 3 (cont'd). Heavy metals content in AMD samples before and after reaction with LGL

LGL Weight (g)	Element	Before Reaction (mg/L)	After Reaction (mg/L)	Percentage Removal of Heavy Metals
2.0	As	6.44 ± 0.34	0.03 ± 0.00	99.5
	Cd	0.26 ± 0.01	0.11 ± 0.00	57.9
	Fe	317.27 ± 13.41	0.32 ± 0.00	99.9
	Cr	0.57 ± 0.02	0.02 ± 0.00	96.5
	Mn	61.63 ± 2.65	40.16 ± 0.30	34.8
	Zn	11.49 ± 0.45	6.30 ± 0.05	45.2
3.0	As	6.44 ± 0.34	0.01 ± 0.00	99.8
	Cd	0.26 ± 0.01	0.07 ± 0.00	73.1
	Fe	317.27 ± 13.41	0	100
	Cr	0.57 ± 0.02	0.02 ± 0.01	96.5
	Mn	61.63 ± 2.65	39.07 ± 0.18	36.6
	Zn	11.49 ± 0.45	2.43 ± 0.01	78.6
4.0	As	6.44 ± 0.34	0.01 ± 0.00	99.8
	Cd	0.26 ± 0.01	0.07 ± 0.03	73.1
	Fe	317.27 ± 13.41	0	100
	Cr	0.57 ± 0.02	0.02 ± 0.00	96.5
	Mn	61.63 ± 2.65	38.26 ± 0.34	37.9
	Zn	11.49 ± 0.45	1.69 ± 0.03	85.3
5.0	As	6.44 ± 0.34	0.01 ± 0.00	99.8
	Cd	0.26 ± 0.01	0.03 ± 0.00	88.5
	Fe	317.27 ± 13.41	0	100
	Cr	0.57 ± 0.02	0.02 ± 0.00	96.5
	Mn	61.63 ± 2.65	37.48 ± 0.16	39.2
	Zn	11.49 ± 0.45	1.14 ± 0.01	90.1
6.0	As	6.44 ± 0.34	0.01 ± 0.00	99.8
	Cd	0.26 ± 0.01	0.03 ± 0.00	88.5
	Fe	317.27 ± 13.41	0	100
	Cr	0.57 ± 0.02	0.02 ± 0.00	96.5
	Mn	61.63 ± 2.65	37.64 ± 0.07	38.9
	Zn	11.49 ± 0.45	1.14 ± 0.01	90.1

Conclusion

LGL is capable to treat AMD by increasing the pH that complies with Standards A and B. The best pH value chosen was 6.11 ± 0.00 by using 5.0 g of LGL at interval time 20 min. LGL is also suitable to be used in reducing heavy metals content in AMD such as arsenic, chromium and zinc by precipitation process. LGL is not suitable to be used for reducing manganese and cadmium content in AMD. More alkaline materials such as hydrated lime, quicklime, sodium hydroxide and so on are suitable to treat these heavy metals. Manganese and cadmium can be precipitated as hydroxide metals at pH 10 [16] and pH range 10.5 to 11 [17], respectively.

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