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Prediction and Remediation of Water Quality in Monitoring Potential of Acid Mine Drainage

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Abstract: Acid Mine Drainage (AMD) associated with both active and abandoned mining operations related to sulfide minerals, oxidation of pyrite affording an acidic solution that contains toxic metal ions. Result shows that pH value of water in Kg. Aur, Chini and Sg. Lembing are acidic with value of 2.81, 4.16 and 3.60 respectively. Maximum concentrations of heavy metals in the study area are: Pb (0.2 mg/L), Cd (0.05 mg/L), Zn (5.1 mg/L), Cu (5.2 mg/L), Mn (10.9 mg/L), Cr (0.2 mg/L), Ni (0.2 mg/L), As (0.005 mg/L) and Fe (202.69 mg/L). Prediction of acid formation using acid-base calculations from all samples shows high potential acid production between 22.84-2500.16 kg $CaCO_3$/tonne. The ratio of Neutralization (NP) with Acid Potential (APP) shows a very low value (ratio<1) Sg. Lembing (0.02), Chini (0.08), Selinsing (0.31) and Kg. Aur (0.81). Analysis from the tank experiment after 30 days shows pH of LFS, bentonite, activated carbon and zeolite change to 6.11, 3.91, 2.98 and 2.71 respectively. Three mine sites experiencing AMD are Kg. Aur, Chini and Sg. Lembing. Active neutralization treatment successfully shows LFS has great potential to control AMD based on their ability to neutralize the pH and remove heavy metals in the mine water. Meanwhile, the second adsorbent material is bentonite followed by activated carbon and zeolite.

Keywords: AMD, Heavy Metals, Acid-Base Accounting (ABA), Remediation

Introduction

Acid Mine Drainage is quite new environmental problem in Malaysia (Madzin *et al*., 2016). Mineral processing of hard rock, metal ores (e.g., Au, Cu, Pb, Zn) and industrial mineral deposits (e.g., phosphate, bauxite) involves the size reduction and separation of the individual minerals. Consequently, the end products of ore or industrial mineral processing are concentrated of the sought-after commodity and a quantity of residue wastes known as tailings (Young *et al*., 2017). Rock waste or tailings from the weathering of pyrite (FeS_2) and sulfide minerals can contribute to Acid Mine Drainage AMD (Johnson and Hallberg, 2005). The potential presence of acidic environment when these rocks contain metal sulfides, especially iron disulfide (FeS2) which is pyrite and or marcasite, they become oxidized by air and water producing Fe^{2+}, H^+ and SO_4^{2-} ions. When these ions get into the solution, sulfuric acid is produced (AMD). Prediction the potential of AMD can be exceedingly challenging and costly due to mineralogy and other factors that are highly variable from site to site (USEPA, 1994). Static and kinetic geochemical tests are commonly used to predict AMD generation. Static tests involve determination of Net-Acid Production Potential (NAPP) and/or Net Acid Generation (NAG) values (expressed in either kg H_2SO_4/t as used here or kg $CaCO_3$/t). NAPP is calculated through Acid Base Accounting (ABA) procedures. Positive NAPP values indicate a potential to generate acid. NAG values are obtained through the reaction of pulverised sample with H_2O_2 to accelerate sulphide oxidation with the resulting liquor titrated with NaOH and NAG (kg H_2SO_4/t) values calculated. Its environmental impact, however, can be minimized at three basic levels: Through primary prevention of the acid-generating process; secondary control, which involves the deployment of acid drainage migration prevention measures; and tertiary control, or the collection and treatment of effluent (Akcil and Koldas, 2006).

The choice of which option to use to remediate AMD is dictated by a number of economical and environmental factors (Barrie and Kevin, 2005). Active

treatment involves regular reagent and labour inputs, while passive treatment only requires occasional maintenance (Jeff *et al.*, 2005). The addition of chemical-neutralizing agent, is an active treatment process to mitigate acidic effluents (Coulton *et al.*, 2003). In general, an adsorbent is assumed as "low-cost" if it needs very little processing, is abundant in nature, or could be a byproduct or waste material from another business (Haider *et al.*, 2014). The use of natural material from clay mineral has undoubtedly become more popular and widely used as an adsorbent especially for removing heavy metal, organic pollutants and nutrients (Abdelaal, 2004). Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated for by inorganic and organic cations from the environment (Konig *et al.*, 2012). The industrial by products could be assumed to be the low-cost adsorbents due to their abundance in nature and less processing requirements. The slag as an alternative adsorbent has been used to remove heavy metals in the environmental field due to its unique properties (Dias *et al.*, 2007; Barakat, 2011). The aimed of this study are to investigate the acid mine drainage potential through analytical tests which is static tests. The characteristic of different adsorbents material (LFS, zeolite, bentonite, kaolinite and active carbon) and the adsorption of heavy metals (Cd, Fe, Mn, Cu, Zn, Pb and Ni) have been investigated in controlling AMD occurrence, improving water quality and to identify immobility mechanism of metals through a series of tank experiments.

Materials and Methods

Mining Site Sampling Procedure

The studies were conducted at four active mining sites and five abandoned mining sites (Table 1). Samples such as water, rock, tailing and soil were collected. Water analysis of in-situ parameters such as pH, dissolved oxygen, potential production, temperature, salinity and conductivity were measured by using Quality meter YSI 656. For water sampling, one liter of water was collected from each sites and preserved by adding ultra-pure acid and then the samples were stored in a cooler box of approximately 4°C before being transported to the laboratory for further analysis. The waste rock samples were collected and put in plastic bag for each site. Meanwhile, tailings and soils were collected from nine sites and for each sampling site, 2-3 kg of the samples were packed and sealed in prewashed plastic bags to maintain its characteristics.

Analysis of Water from Mining Site

The water analysis procedures are obtained from following steps. Firstly, the AMD solutions were filtered through a membrane of 0.45μm pore to get the clear effluent before tested. Heavy metal elements (Cd, Pb, Zn, Cu, Mn, Ni, As and Cr) and major cation (Ca, Mg, K, Na as well as Fe) were determined by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) model of Perkin Elmer Elan900. Meanwhile, for major anions (sulfate and chloride) analysis was conducted by filtered the solution through 0.2 μm pore size. Metrohm 850 Professional Ion chromatography with chemical suppression was performed to measure sulfate and chloride anion contents

Analysis of Rock and Soil

Physical-chemical tests such as pH, neutralization potential, total sulfur of rock and soil were determined using standard method of USEPA (Sobek *et al.*, 1978). A representative 250 g portion was prepared by splitting, dried and pulverized to less than 0.25mm for the titration test. The pH of the samples obtained by adding 10g of soil and mixed with 25 ml distilled water and then stirred with spatula continuously. The pH value was measured by using Hanna measurement pH instrument with the ratio of water and sample was 1:2.5. The pH meter calibrated with buffer solution at pH:4 and pH:7. Total sulfur in the sample represents the maximum potential of acidity followed by E1915-97 method (ASTM 2000a) (Smith *et al.*, 1974).

Table 1: The parameter and characteristic of the mining sites

Mining sites	GPS coordinate	Type of minerals	Status until 2013	Types of site
Bukit Ibam	N03'10'12.8"/E102'58'05.5"	Iron	Active	Pond
Kg. Aur (Upper)	N 03'08'11.8"/102'57'38.9"	Hematite	Abandoned	Stream
Kg. aur (Bottom)	N03'08'05.3"/E102'58'07.1"	Hematite	Abandoned	Stream
Chini	N03'23'34.9"/E102'56'46.1"	Manganese	Abandoned	Pond
Sungai Lembing	N03'54'35.2"/E103'01'51.1"	Tin	Abandoned	Stream
Kuari JKR Kg. Awah	N03'29'51.8"/E102'32'30.4"	Andesite	Abandoned	Pond
Kuari Kota Gelanggi	N03'53'09.1"/E102'28'42.6"	Limestone	Abandoned	Pond
Kg. Besul	N04'00'09.4"/E102'18'37.3"	Iron	Active	Pond
Selinsing	N04'14'54.2"/E101'47'14.5"	Gold	Active	Pond
Batu Malim	N03'58'02.1"/E101'46'27.5"	Iron	Active	Pond

Analysis of Tailings

Toxicity Characteristic Leaching Procedure (TCLP) for these soils was determined using USEPA Method 1311 (1999). After sampling, holding time for metal have 180 days until leaching, except for mercury where leaching must start within 28 days. 10 g of soil was mixed with glacial acetic acid (adjusted to pH 4.93 with 1 N NaOH) at 20 L kg^1 in polypropylene bottle. Then the bottle was agitated with junior orbital shaker at 200 rpm for 18 h. After 18 h, the liquid was filtered through 0.45 µm membranes, acidified with concentrated nitric acid and stored in amber vials at 4°C. TCLP tests are completed in a short (18-h) contact duration. The metal concentrations such as As, Ba, Cd, Cr (VI), Pb, Se, Ag, Hg were determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Prediction of AMD

Static tests are geochemical analyses of sulfide waste which are used to predict the potential of a waste sample to produce acid. A significant part of the static test is Acid Base Accounting (ABA), which refers to the numerical data used to predict acid generation. The three components of the ABA are: (i) Determination of acid production; (ii) Determination of acid consumption; and (iii) Calculation of net acid production or consumption using the data from (i) and (ii). Here, (i) Determination of acid production from tailings samples deals with the measurement of total sulfur, which is the main goal of research. Acid Production Potential (APP) based on the assumption that two moles of acid will be produced for each mole of sulfur present in the mine waste. The total sulfur content in percent is multiplied by 31.25 to yield the APP in units of tons acidity as $CaCO_3$ per 1000 tons rock (or equivalently, kg $CaCO_3$/metric ton). Neutralization Potential (NP) test was performed to determine the quantity of acid-consuming minerals in a sample (Sobek *et al.*, 1978). The NP test started with "a fizz test" which was done by adding one or two drops of 25 % HCl solution to about 0.5g of sample and observing the degree of effervescence. The fizz test was used to rank sample as none, slightly, moderate and strong. The appropriate amount and concentration of HCl was added to 2.0g of sample in a flask and placed on a hot plate until the sample was just beginning to boil. The flask was taken off the heat and swirled intermittently until no more effervescence was observed. More distilled water was added to make a total volume of 125 ml. After heated for 1 min, the sample was left to cool down above room temperature before titration. The sample is then titrated with 1.0 N sulfuric acid until a pH of 7.0 is reached. The pH 7 was selected since this pH represents the amount of acid that a mine waste could neutralize while maintaining drainage pH in a range that meets quality standards. Prediction of acid is determined by the Net Neutralization Potential (NNP), which is the difference between these values (NNP = NP-APP).

Typically, this difference is initially assessed by Acid–Base Accounting (ABA) to determine the Net Acid Production Potential (NAPP) of a sample. ABA test was developed by Smith *et al.* (1974) and subsequently modified by Sobek *et al.* (1978) to evaluate the acid producing capacity of coal mine wastes. Sobek *et al.* (1978) indicated that waste would produce acid if and only if NNP was less than -5 kg $CaCO_3$/ ton.

Treatment Materials Preparation

The preparation of raw Ladle Furnace Slag (LFS) material start by air-dried at room temperature for one week. The dried and raw-shaped of LFS then was ground using a mechanical grinding and mortared manually to form fine-pollen of material before experimental work start. Meanwhile the natural materials used in this research originated from different places, for example kaolinite sample was obtained from Perak, bentonite sample from Australia, zeolite sample from Indonesia and active carbon originated from Seremban, Negeri Sembilan respectively. These dried-sample were sieved using a manual sieved (standard test sieve ASTMII Specification) to obtain particle size of 0.063 mm. The sample collected are usually characterized using several laboratorial techniques, such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). ICP-AES, XRF and SEM-EDX are usually applied to analysis the major elements present in the sample (Nunes *et al.*, 2016).

Treatment of AMD

The experimental tank was designed with silica glass materials (18×17.5×17.5). Each tank was set up with 5 liters of synthetic water. The synthetic solutions contain of high concentrations of Fe(II), Mn, Pb(II), Cu(II), Zn(II), Cd(II) and Ni(II) for 251, 572, 561, 840, 753, 647 and 754 mg/L respectively with initial pH at 2.4. Only four types of adsorbents used for treatment process except kaolinite due to treatment weaknesses. Adsorbents were weighed out for 100g and put into cotton pot before ready for treatment process. The tanks were run by magnetic stirrer FAVORIT with 200 rpm nonstop for 30 days.

Results

Characterization of AMD Samples

Table 2 indicates the results of pH, conductivity (EC), potential production (Eh), Temperature (T), Total Dissolved Solid (TDS), Dissolved Oxygen (DO) and salinity. Field data of AMD is in acidic phases at pH 2.81-4.16 for Kampung Aur, Sungai Lembing and Chini respectively. The highest reading of D.O was recorded at Kg. Besul at 10.06 mg/L and the lowest value recorded at Kg. Aur (7.45 mg/L). The value of D.O for water pollution index in clean water class V is more than 1 mg/L and all mining sites were considered safe due to the value of dissolved oxygen.

Table 2: In situ water quality parameters of mine water

Mining Sites	Temp. (°C)	pH	DO (mg/L)	Eh (mV)	Salinity	Conductivity (μs/cm)	TDS (g/L)
Bukit Ibam	29.6	7.90	8.44	-37.7	0.65	911.67	0.84
Kg. Aur (Upper)	29.9	2.81	7.45	244.0	1.46	1699.67	1.57
Kg. Aur (Lower)	28.9	3.17	7.40	233.1	0.88	1166.00	1.12
Chini	29.7	4.16	8.05	195.8	0.20	312.00	0.27
Sungai Lembing	29.6	3.60	8.36	153.0	0.09	135.33	0.12
Kuari JKR Kg. Awah	33.3	7.89	9.27	-37.4	0.16	260.00	0.22
Kuari Kota Gelanggi	33.5	7.66	8.14	-31.1	0.15	218.00	0.20
Kg. Besul	31.3	7.61	10.06	-20.6	0.33	485.67	0.43
Selinsing	31.6	6.60	8.08	-16.7	0.32	438.00	0.43
Batu Malim	35.8	7.46	7.47	-19.0	0.04	67.00	0.06

The potential production (Eh) showed a high value were recorded at Kg. Aur, Chini and Sungai Lembing (153.0, 195.8 and 244.0 mV) respectively while electrical conductivity was recorded between 438.0 to 1699.67μs/cm in some places respectively. Table 3 illustrates the average of concentration of heavy metals such as Pb, Cd, Zn, Cu, Mn, Cr, Ni and As obtained from all mining sites and calculated concentration is shown in Fig. 1. The concentration of lead, Pb(II) found very high at Kg. Aur upper (0.215 mg/L) while the concentration of cadmium and zinc were highest recorded at Sungai Lembing (0.047 and 5.07 mg/L respectively). AMD was strongly acidic and contained significant levels of metal ions, especially Fe.

The acidic characteristic of the AMD results from the percolation of water through sulfide minerals generally pyrite, which oxidizes and dissociates when in contact with air and water. The concentration of Fe was found very high at Kg Aur (bottom part) of 202.69 mg/L, Kg Aur (upper part) of 129.43 mg/L, while the lowest content of Fe found at Batu Malim of 0.05 mg/L. There were no significant differences between mine waters for the concentration of kalium while other metals (Pb, Zn, Cr, Cd, Cu, Ni and As) show significantly differences in terms of concentration. The lead and chromium exceeded for concentration of standard WQA 2000 in Kg. Aur, Sungai Lembing, Selinsing and Chini and the concentration of cadmium in Sungai Lembing exceeded the standard too. The content of heavy metal at Kg. Aur and Sungai Lembing displays very low concentration of Cu but high content of Mn. The mean values for Mn was higher at Chini with concentration of 36.91 mg/L. The anion values of sulfate were found maximum at lower part of Kg Aur (5180.86 mg/L) while very minimum at Cheroh (20.22 mg/L). Meanwhile for chloride was found very high at lower part of Kg Aur (48.56 mg/L) but the concentration at Sungai Lembing was very low (1.21 mg/L).

AMD Prediction

Table 4 lists AMD prediction results using acid-base accounting method for each mine sites. The values of pH identified the host rock of each mining sites. Kg. Aur has pH value 2.34 which host rock is hematite and Chini with pH value of 2.00 which host rock is manganese. Only five mining sites have sulfur content

which are Bukit Ibam, Kg. Aur, Chini, Selinsing and Sungai Lembing with total values of APP of 22.86 kg CaCO$_3$/ton, 50.79 kg CaCO$_3$/ton, 924.27 kg CaCO$_3$/ton, 22.84 kg CaCO$_3$/ton and 2500.16 kg CaCO$_3$/ton respectively. Analyses of rock samples from other sites which are JKR Kg. Awah, Kota Gelanggi, Kg. Besul and Gelanggi have not detected any sulfur content. From total sulfur analysis, the highest value of total sulfur content recorded at Sungai Lembing which are 2500.16 kg CaCO$_3$/ton. The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid (Smith *et al.*, 1974). The values of Neutralizing Potential (NP), obtained from the titration test in decreasing order, Chini > Bukit Ibam > Kg Aur > Selinsing > Sungai Lembing were calculated as 337.43 kg CaCO$_3$/ton, 159.63 kg CaCO$_3$/ton, 41.18 kg CaCO$_3$/ton, 13.38 kg CaCO$_3$/ton and 7.32 kg CaCO$_3$/ton respectively. Meanwhile the classification of acid-bases for rock walls were found at low values of NP/APP at Kg. Aur, Chini, Selinsing and Sungai Lembing of 0.81, 0.37, 0.59 and 0.003 respectively as summarized in Fig. 2.

Toxicity of Tailing and Soil

The Toxicity Characteristic Leaching Procedure (TCLP) test is used to determine the mobility of toxic contaminants present in waste materials and to define hazardous wastes under the Resource Conservation and Recovery Act (RCRA), 1984). The results from TCLP experiment showed that the concentration of As leached from sediment in the Kg. Aur bottom samples after an 18h extraction time was 7.955 mg/L, which is exceeding the current maximum US EPA TCLP value for As. This would be characterized as a hazardous waste. The comparison of the sample between sediment in the Kampung Aur (bottom part) and tailing in the Sungai Lembing show different result of TCLP.

Table 5 identified heavy metals content with the highest concentration of Pb (17.42 mg/L) at Sungai Lembing tailing and the lowest concentration found at Kg. Aur (bottom part), which is 1.21 mg/L. The concentration of Cd found in Sungai Lembing tailing was 1.3 mg/L and soil in Sungai Lembing showed below the limitation value of concentration.

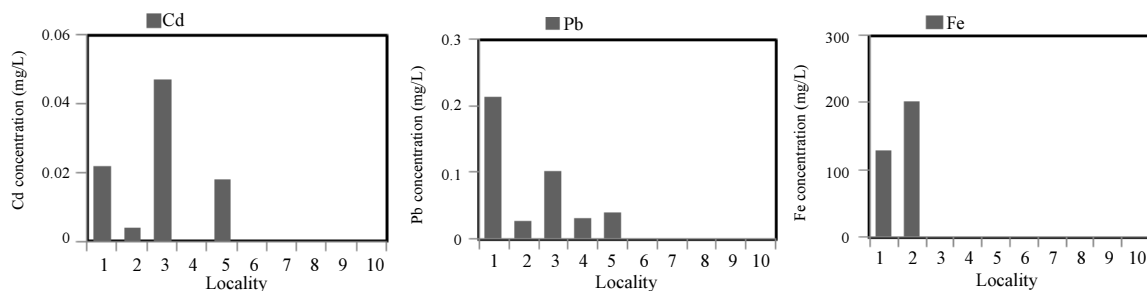**Table 3:** The concentration values of heavy metals in mine water as compared to EQA and WQS standard

Locality/symbol	1	2	3	4	5	6	7	8	9	10	Environment quality act	Water quality standard
Element (mg/L)/ Locality	Kg Aur Upper	Kg Aur Bottom	Sungai Lembing	Selinsing	Chini	Kg. Besul	Kuari Kota Gelanggi	Kuari Kg Awah	Bukit Ibam	Batu Malim	EQA 1997	WQS 2000
Pb average n = 9	0.215 (0.199-0.22)	0.028 (0.027-0.032)	0.102 (0.098-0.103)	0.031 (0.024-0.035)	0.040 (0.037-0.047)	0.000 (-)	0.000 (-)	0.000 (-)	0.0002 (0-0.004)	0.000 (-)	0.1	0.01
Cd Average n = 9	0.022 (0.012-0.025)	0.004 (0.004-0.004)	0.047 (0.044-0.05)	0.000 (-)	0.018 (0.015-0.019)	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	-	0.03
Zn Average n = 9	1.005 (0.998-1.00)	0.557 (0.483-0.613)	5.070 (4.77-5.554)	0.783 (0.566-0.845)	1.685 (0.999-1.037)	0.007 (0.002-0.001)	0.001 (0.0005-0.001)	0.000 (-)	0.012 (0.006-0.021)	0.004 (0.002-0.008)	2.0	0.3
Cu Average n = 9	1.185 (0.988-1.100)	1.065 (0.999-1.117)	5.232 (4.978-5.55)	0.000 (-)	0.154 (0.138-0.197)	0.003 (0.002-0.001)	0.004 (0.002-0.006)	0.003 (0.001-0.005)	0.005 (0.0006-0.010)	0.000 (-)	0.2	-
Mn Average n = 9	2.157 (1.922-2.00)	3.802 (3.335-4.074)	10.945 (10.14-11.70)	2.778 (2.111-2.34)	36.914 (33.58-39.24)	0.024 (0.015-0.031)	0.001 (0.001-0.001)	0.006 (0.001-0.011)	0.536 (0.532-0.556)	0.052 (0.027-0.068)	-	0.1
Cr Average n = 9	0.026 (0.015-0.029)	0.031 (0.025-0.048)	0.0182 (0.013-0.027)	0.029 (0.019-0.033)	0.009 (0.006-0.012)	0.010 (0.001-0.016)	0.023 (0.016-0.036)	0.010 (0.005-0.015)	0.017 (0.005-0.042)	0.171 (0.163-0.177)	0.05	0.05
Ni Average n = 9	0.036 (0.026-0.037)	0.038 (0.034-0.041)	0.126 (0.120-0.131)	0.169 (0.13-0.177)	0.025 (0.022-0.027)	0.005 (0-0.008)	0.007 (0.005-0.012)	0.002 (0.002-0.003)	0.011 (0.008-0.011)	0.014 (0.008-0.018)	0.2	-
As Average n = 9	0.003 (0.001-0.004)	0.002 (0.001-0.002)	0.002 (0.002-0.002)	0.005 (0.002-0.006)	0.003 (0.002-0.003)	0.000 (-)	0.001 (0-0.001)	0.001 (0.0005-0.001)	0.001 (0.001-0.001)	0.000 (-)	0.05	0.01
Ca	12.752	0.000`	4.882	49.462	1.010	34.031	18.919	16.385	51.728	2.276	-	-
Mg	8.584	93.755	2.813	27.478	0.4133	9.128	9.159	10.707	56.029	5.346	-	-
K	1.738	7.861	0.584	3.531	1.9275	1.685	0.3003	0.475	10.992	0.836	-	-
Na	2.501	15.788	15.788	11.512	1.710	25.224	0.633	6.742	3.987	90.092	-	-
Fe Average n = 9	129.433 (115.20-130.00)	202.69 (180.82-213.47)	1.203 (0.974-1.532)	0.203 (0.156-0.244)	0.269 (0.188-0.984)	0.364 (0.27-0.700)	0.345 (0.29-0.77)	0.142 (0.118-0.165)	0.525 (0.488-0.579)	0.050 (0.032-0.060)	1.0	0.3
SO_4^{2-}	3179.6	5180.86	75.67	247.89	48.94	220.52	87.58	65.86	718.69	20.22	0.5	250
Cl^-	21.52	48.56	1.21	3.68	2.36	9.02	4.26	2.38	6.39	1.5	2.	250

Table 4: The AMD prediction results of Acid-Base Accounting method for each mine sites

Locality	Total of APP (kg CaCO3/ton)	Total of NP (kg CaCO3/ton)	NPP (NP-APP)	NP/APP	pH	Samples
Bukit Ibam	22.86	159.63	136.77	6.98	8.00	Ore
Kg. Aur	50.79	41.18	-9.61	0.81	2.34	Hematite
Chini	924.27	337.43	-586.84	0.37	2.00	Manganese
Selinsing	22.84	13.38	-9.46	0.59	7.90	Slate
Sungai Lembing	2500.16	7.32	-2492.84	0.003	2.90	Tailings

Table 5: The concentration of As, Cd, Cr and Pb for TCLP test

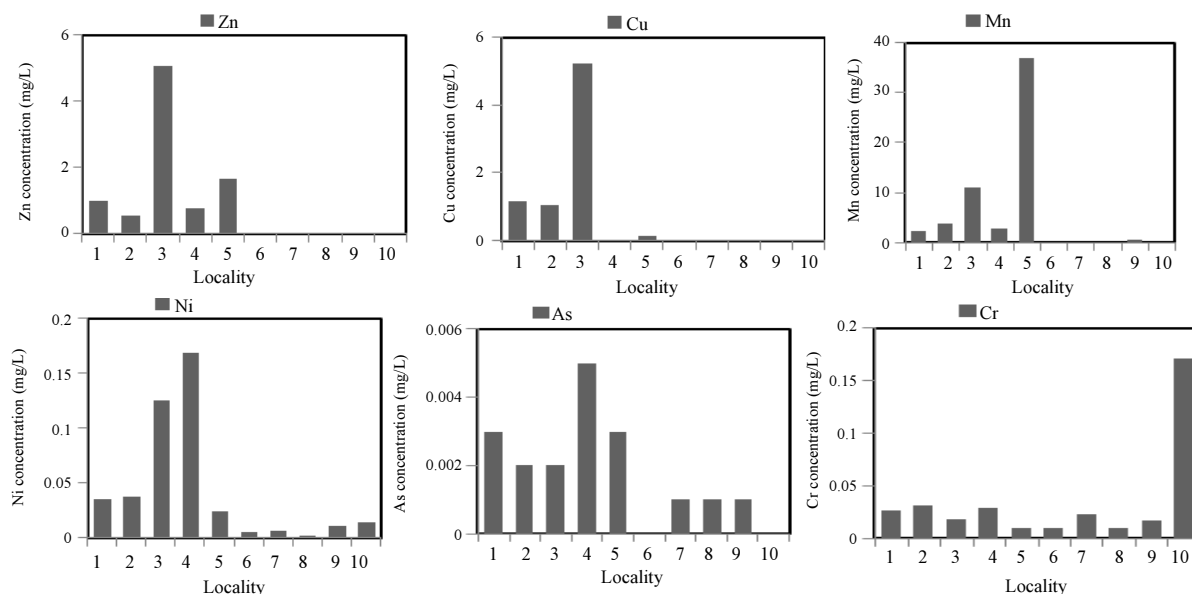| TCLP	Sungai Lembing soil (mg/L)	Sungai Lembing Tailing(mg/L)	Kg. Aur bottom (mg/L)	USEPA (mg/L)
Arsenic	1.86	0.814	7.955	5
Cadmium	0.319	1.3	0.096	1
Chromium	0.213	0.35	0.223	5
Lead	3.864	17.417	1.207	5

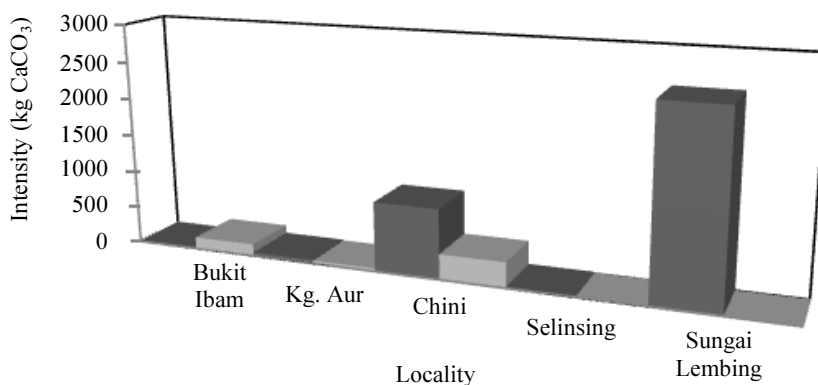**Fig. 1:** The concentration values of heavy metals (mg/L) for each locality

Fig. 2: The concentration of NP and APP for each locality

Characterization of Treatment Material

The major elements from treatment test are analyzed by XRF. Table 6 summarized LFS has the highest percentage of CaO which is 52.86%, while bentonite, zeolite and kaolinite contained of highest percentage of SiO of 53.00%, 65.23% and 77.99% respectively. Active carbon showed a very lowest value of elemental phases (< 5%). XRF analysis showed the lowest elemental composition of LFS was SiO (5.93%) while bentonite and zeolite showed the similar lowest elemental composition which is Fe_2O_3 of 2.88 and 2.66% respectively. Figure 3 identified SEM images of LFS, bentonite, zeolite and active carbon. SEM image of LFS is characterized by large clusters of radiating tetragonal prisms cemented together with homogeneous particles with rough surfaces. SEM images of bentonite and zeolite characterized by similar platy textures in different particle sizes. SEM image of active carbon showed a rough and nonhomogeneous

structures with size of particles ranging from 1 mikrometer to 100 mikrometer. Figure 3 were SEM images for (a) ladle furnace slag (magnification 500x) (b) bentonit (magnification 500x) (c)active carbon (magnification 500x) and (d)zeolite (magnification 2000x).

Effect of pH

The variations of pH values with time identified as Fig. 4. The synthetic solution present low pH values approximately 2.39-2.4 at the beginning. At the beginning, LFS analysis showed significantly increase of pH value (4.35) while other adsorbents showed slightly increase 2.41-2.71. High content of CaO in LFS increased the alkalinity of solution. Moreover, at days 30, synthetic solution contains LFS showed nearly to neutral pH (6.11) compared to others which are bentonite 3.91), active carbon (2.98) and zeolite (2.71) still in acidic phases respectively.

Table 6: Major element for treatment materials

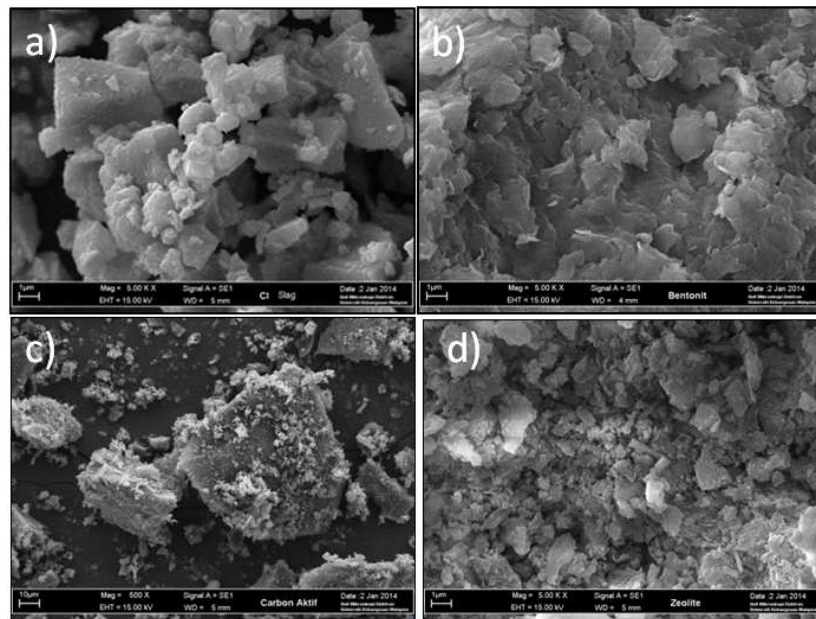| Major element (%)	LFS	Bentonite	Zeolite	Kaolinite	Active Carbon
SiO_2	5.93	53.00	65.23	77.90	2.34
$TiO2$	0.15	0.34	0.42	0.55	*n.a*
Al_2O_3	26.92	16.91	12.15	13.00	*n.a*
Fe_2O_3	1.22	2.88	2.66	0.98	0.27
MnO	0.04	0.01	0.04	0.01	0.02
MgO	7.73	3.06	0.83	0.31	0.12
CaO	54.86	2.09	3.55	0.19	1.91
Na_2O	0.05	1.51	1.44	0.05	0.02
K_2O	0.08	0.36	0.93	1.67	1.99
P_2O_5	0.01	0.04	0.04	0.03	0.07
L.O.I	0.32	21.45	14.30	4.80	4.17
Jumlah	95.30	101.70	101.60	99.65	-

Fig. 3: SEM images for (a) ladle furnace slag (magnification 500×) (b) bentonite (magnification 500×) (c) active carbon (magnification 500×) and (d) zeolite (magnification 2000×)
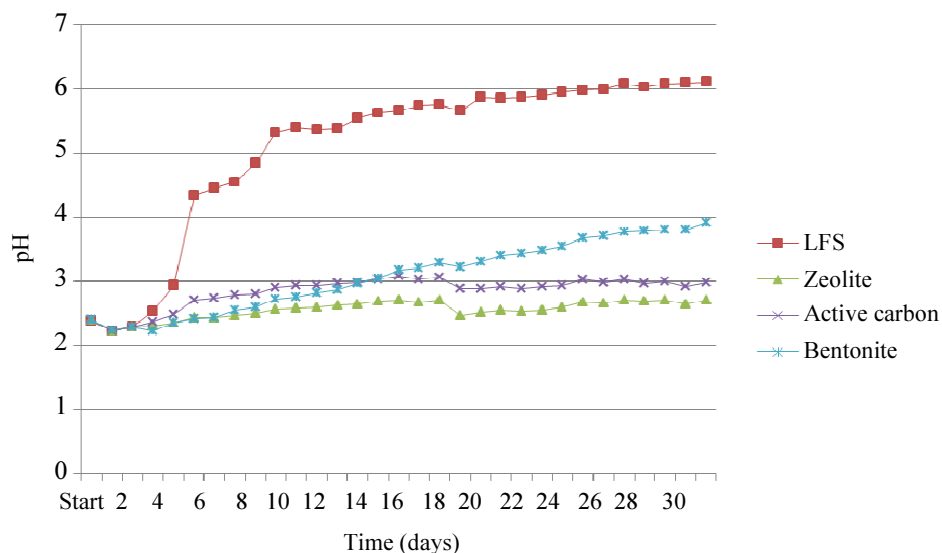

Fig. 4: The variations of pH values of LFS, bentonite, active carbon and zeolite during stirring tank operation for 30 days
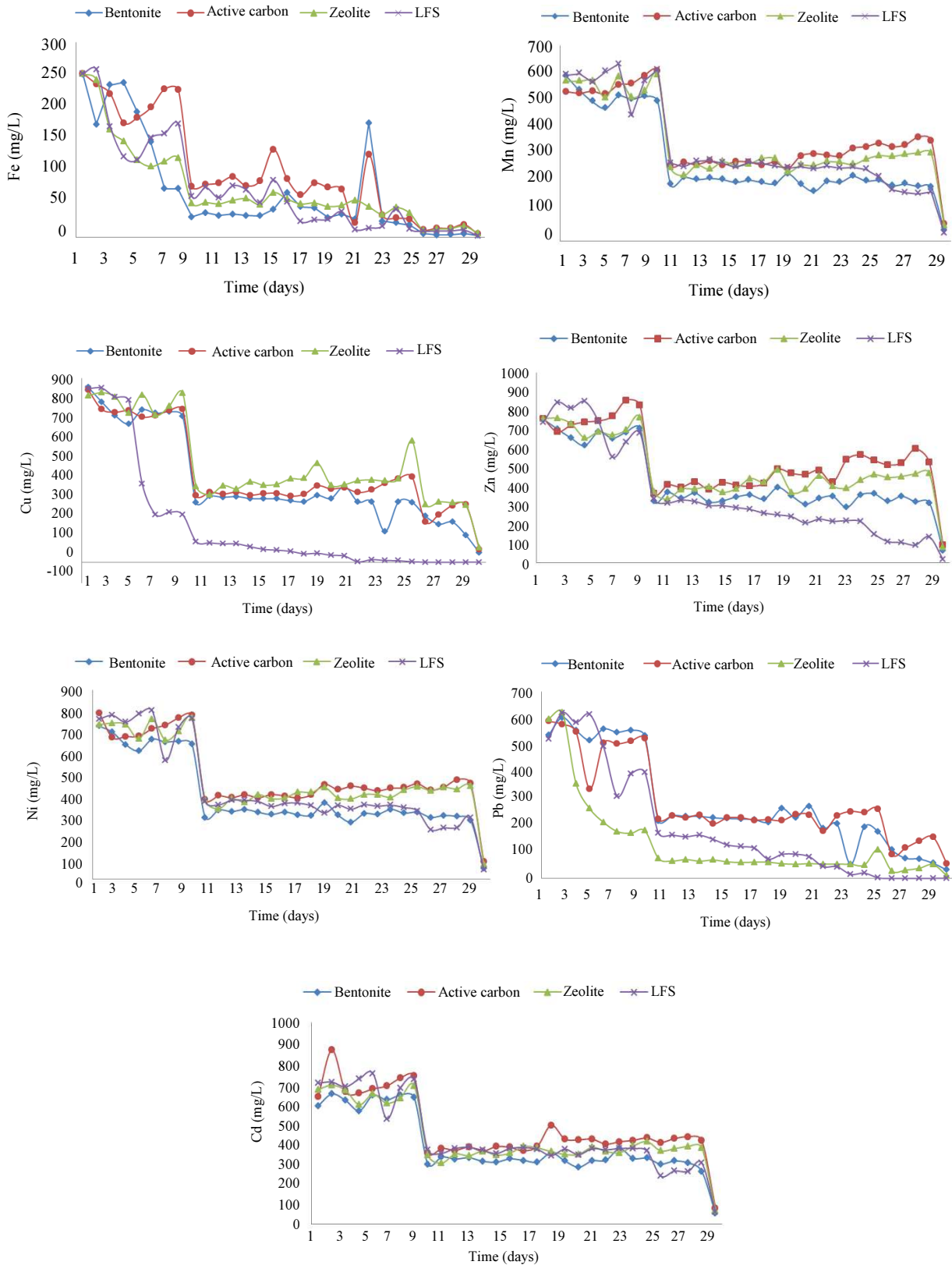
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Fig. 5: Variation of Cd, Fe, Mn, Cu, Zn, Pb and Ni concentrations during stirring tank operation for 30 days

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Removal of Metals from Tank Experiment

Figure 5 indicates the concentration of heavy metals with respect to time in the effluents from stirring tank. The pattern of heavy metals removal were decreasing through time. At the end of the tank experiment showed Fe concentration decreased from initial concentration of 251.34 to 5.84 mg/L (bentonite), 11.26 mg/L (LFS), 17.27 mg/L (zeolite) and 19.74 mg/L (active carbon) respectively. Mn concentration were decreased from initial concentration of 572.63 mg/L to 176.35 mg/L (LFS), 192.24 mg/L (bentonite), 313.90 mg/L (zeolite) and 360.44 mg/L (active carbon). The initial concentration of Cu decreased from 840.19 mg/L to 0.40 mg/L (LFS), 132.02 mg/L (bentonite), 278.60 mg/L (zeolite) and 281.49 mg/L (active carbon). For Zn, the initial concentration decreased from 753.77 to 138.14 mg/L (LFS), 316.98 mg/L (bentonite), 473.04 mg/L (zeolite) and 529.42 mg/L (active carbon), while the concentration of Pb decreased from 561.58 to 0.41 mg/L (LFS), 51.77 mg/L (bentonite), 56.92 mg/L (zeolite) and 154.74 mg/L (active carbon) respectively.

Discussion

Based on the result in Table 2, the pH values recorded very low at Kg Aur, Chini and Sungai Lembing. Meanwhile, Kg. Aur, Chini and Sungai Lembing have the highest value of Eh showed solution that accept more proton and undergoes an oxidation process. According to Sangita and Bably (2010), the low pH of discharge mine water results in the further dissolution of minerals and release of toxic metals, when it allowed getting discharge into other water bodies. The value of pH can be as low as 2 and continues to be an important water pollution problem in mining industry around the world (Tsukamoto and Miller, 2004; Sangita and Bably, 2010). The conductivity of the water in the studied was found high. This high conductivity in the water is an indication of its effect on the water quality. Changes in conductivity were not always coincident with changes in Eh and pH, indicating that conductivity may be a more sensitive tool for locating specific zones focus on sulfate reducing bacteria activity (Lyew and Sheppard, 2001). TDS indicates the general nature of water quality or salinity. Based on TDS classification, it can be said all water in the mining area except at Batu Malim where brackish water. Maximum value of sulfate ions at lower part of Kg. Aur exceeds WHO (2011) limited set at 250 mg/L. For example, as a result of weathering of oxidized sulfide scarlet precipitation can be found up to a thousand meters from the AMD polluted river (Jennings *et al.*, 2008). An excess of chloride ion in water is usually taken as an index of pollution. The high chloride content of water may have

originated from natural sources such as rainfall and the dissolution of fluid inclusions.

Fe, Na, K, Ca and Mg were the major cations for the current study and showed significant differences between all samples. Due to the lower pH, the higher oxidation process, hence value of Fe will be higher. Fe was found highest in areas with low pH and found low in areas with high pH. Hallberg (2010) stated due to the low pH, the solubility of the toxic metals contained in the AMD keeps up at a high level thus permits their dispersion into the environment. The decreasing of pH could be attributed to the oxidation of H_2S and Fe(II). Calcium and sulfate concentration decreased as the precipitation proceeded. Precipitation using alkaline reagents for this research is the most widely used treatment method for removing metals as hydroxides (Johnson and Hallberg, 2005; Balintova and Petrilakova, 2011). The decrease in the chloride concentration probably could be ascribed due to the formation of some metal chloride. Thus, water reservoir in Chini has high value of Mn compared to others. Acidic water facilitates the movement of Mn that easily soluble in acidic condition. In another place, pH values closer to 9.0, manganese ions precipitate as manganese hydroxide, Mn $(OH)_2$ allowing its removal (Da Silveira *et al.*, 2009). The concentration of Ni and as were found safe for all water samples.

Prediction of AMD was calculated from APP and result recorded from Table 5. The value of NP/APP is below than 1, interpreted as high potential for acid production. Kg. Aur, Chini, Selinsing and Sungai Lembing have been identified as having high acid generation potential (50.79-2500.16 kg $CaCO_3$/ton) compare to neutralization potential. ABA considers two factors, total S and NP, assumed to represent FeS_2 and $CaCO_3$ (Sobek *et al.*, 1978). Total S can consist sulfide, sulfate and organic sulfur components and acid can be produced by each of these. Pyrite generally is the acid producer and Cravotta (1991) have shown that the dissolution of iron and aluminium-sulfate minerals and the subsequent hydrolisis of iron and aluminium can produce substantial quantities of acidity. Harvey and Dollhopf (1986) have suggested that some forms of organic S also may be acid-producing. Although there were many pyrite minerals in the mining site of Bukit Ibam, AMD did not occur as they were naturally neutralized by calcite minerals. Previous studies in Penjom showed that drainage will remain neutral to basic if the rate of acid consumption equals or exceeds the rate of acid production (Mohd Syahrir and Seong, 2012). Smith and Brady (1990) evaluated if the value of NNP is less than zero, the acid-producing potential of the rock exceeds its neutralization potential and if mined, therefore would be expected to produce AMD. Four localities except Bukit Ibam showed negative values of NPP, then the potential exist for the waste to form acid as suggested by USEPA (1994). The values of ABA for Bukit Ibam have lower risk for the formation of acid mine drainage. Brodie *et al.* (1991) suggested if the ratio

is greater than 3:1, experience indicates that there is lower risk for acid mine to develop, meanwhile samples with a ratio of 1:1 or less are potentially to generate acid.

From TCLP analysis, hazardous waste was identified at Sungai Lembing and Kg. Aur. This is due to the fact that As element in Sungai Lembing had high concentration that exceed the limitation. As concentration in tailing at Sungai Lembing and Pb in Kg. Aur were mobile in characteristic. Exceed value concentration of TCLP element showed element was mobility and of great danger to environment. Hence, labeled as hazardous waste. The proportion of metals leached by the TCLP depends on a sludge's neutralization potential. A sludge with small neutralization potential is incapable of neutralizing all the acid added and the resultant low pH will cause a substantial proportion of the metals present to be leached (Danny and John, 2006).

The immobilization of heavy metal ions from aqueous solutions is quite a complicated process, consisting of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface (Rios *et al.*, 2008). The removal of heavy metals from AMD using different types of adsorbent materials. All sorbents produced similar trends of removal the heavy metals with an abrupt decrease within 8 days. LFS is the best material for absorption of Zn, Mn and Cu in the contaminated water followed by bentonite, zeolite and active carbon. Various researchers including Ziemkiewicz and Skousen (1998; Simmons *et al.*, 2001; Ochola and Moo-Young (2005) have identified steel slag as a suitable candidate to remediate waters contaminated by Acid Mine Drainage (AMD), since it has been shown to have a significant acid neutralizing potential that can be exploited to precipitate out a majority of dissolved metals by increasing solution pH. The Acid Neutralization Potential of steel slag was determined to be approximately 83% as calcium carbonate ($CaCO_3$) (Ochola and Moo-Young, 2005). Meanwhile, bentonit was the best to adsorb more Ni, Fe and Cd. The concentration of heavy metal was decreased greatly due to owning of precipitation, co-precipitation and huge absorbency. Therefore, the utilization of LFS can achieve the purpose to neutralize the high acidity, minimize the release of heavy metal and improve the water quality of drainage.

Conclusion

Analysis was done at the mine which has a watershed. Water is an important indicator to determine the level of acidity of mine drainage. Overall, Kg Aur, Cini and Sungai Lembing found very acidic with low pH and contain high concentration of heavy metals. Therefore, the acidity and neutralization test were

applied for waste rock, tailings or soil at the mining site. Acid-base accounting showed the possibility of field sites to form and produce acid especially for Sungai Lembing with the highest value of APP. TCLP element was made to test the nature of mobility and thus labeled as hazardous waste. Sungai Lembing and Kg. Aur have hazardous waste of Pb and As elements respectively. The AMD levels are identified from low pH and sulfate ions or high of heavy metal. Supported by this static test, results showed that the potential mine suffered of excessive acid production. Overall, AMD identified from all these tests at Kg Aur, Sungai Lembing, Selinsing and Chini. The most dangerous among others is Sungai Lembing and if no action is made, it can affect surrounding area with high generation of acid potential. There are known treatment methods which can be applied before the AMD situation can worsen and consequently source river pollution. By conducting continuous tank experiment tests for about 30 days using synthetic solution prepared, it was found that by product material such as LFS and natural material such as bentonite can effectively adsorb and remove various heavy metals simultaneously. Besides, these adsorbents can also efficiently neutralize the acidic drainage due to its high alkalinity production by calcite dissolution.

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Author's Contributions

Nur Athirah Mohamad Basir: Conducting the experimental work and drafting this paper

W.Y. Wan Zuhairi: Is the main supervisor of the study and revise the article.

Nuur Hani Mohammed, Mustapha Atta and Nur Aishah Zarime: Revise the article.

Ethics

This article is an original and contains unpublished materials. All authors have read and approved this manuscript and no ethical issues involved.

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