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Evaluation of the Potential of Boiler Ash from Palm Oil Mill as an Alternative Material for the Improvement of Acid Coal Main Drainage

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Abstract

The study aimed to evaluate the potential of boiler ash from palm oil mills to improve the quality of acid mine drainage (AMD). The experiment was conducted using boiler ash with five doses of 0, 3, 6, 9, 12, and 15 mg. Quicklime was used as a comparison material with doses of 0, 0.02, 0.03, 0.05, 0.1, and 0.3 mg. Boiler ash and quicklime were added to each 500 mL AMD. The parameters of the AMD quality measured were pH, dissolved iron (Fe) and manganese (Mn), and the precipitates of Fe and Mn. The results showed that the addition of boiler ash and quicklime into AMD increased the pH and decreased the concentration of dissolved Fe and Mn and increased the precipitate of Fe and Mn. The pH value of AMD increased with increasing doses of boiler ash and quicklime. An increase in the pH value was followed by a decrease in the dissolved Fe and Mn and anincrease in the Fe and Mn precipitate. The highest pH values, Fe and Mn precipitates, and the lowest dissolved Fe and Mn were obtained by the treatment of 15 mg/L boiler ash and 0.3 mg/L quicklime. The boiler ash showed promising potential as an alternative neutralizing reagent to improve AMD even though the amount of boiler ash needed to repair AMD was more than quicklime.

Keywords: Acid mine drainage, Boiler ash, Quicklime

Introduction

Acid mine drainage (AMD) is wastewater from coal mining activities that is chategorized as strong acid and corrosive. Therefore, it can be dangerous to the environment, especially to the aquatic environment. This wastewater is produced from an active or abandoned mine. The formation of AMD occurs when metal sulfide compounds present in metal precipitates, coal seams, or coal bedrock layers are exposed and oxidized [1]. Pyrite (FeS_2) is the main source of AMD because pyrite is the main sulfide mineral in coal and metal ores as well as in the earth's crust [2]. Pyrite, when exposed to the air and water releases water-soluble components such as Fe^{2+}, SO_4^{2-} and H^{+}. The resulting Fe^{2+} ion is oxidized to Fe^{3+} which then undergoes hydrolysis to form Fe oxide followed by the release of some acids [3].

The acidity of AMD can reach a very low pH of around 2-3 with high concentrations of Fe, Mn, Al, and SO_4^{2-} anions, as well as other metals [4, 5]. Acid water originating from the oxidation of pyrite compounds then reacts with rocks and can contribute large amounts of SO_4^{2-} and toxic metals to drainage water, causing environmental damage to the waters, lakes, groundwater, and soil [6] and inhibitingthegrowth of aquatic plants and plants around them [7]. Another negative effect of AMD can cause corrosion of machine tools such as engine parts of turbines [5]. Therefore, an appropriate method or technology is needed for the management of AMD. The management must be able to produce water which can be a source of life for organisms and can be used for various uses.

The development of suitable solutions for managing AMD is necessary to minimize and mitigate the danger of environmental contamination resulting from excessive AMD formation. AMD can be managed using a variety of techniques, most of which fall into one of two categories: active system or passive system. Anaerobic wetlands, vertical flowing wetlands, and aerobic wetland ponds are a few examples of passive management techniques. However, this passive treatment system requires a large area of land which is the weakness of the passive method[8].The active management method involves the addition of alkali to increase the pHof AMD. The addition of alkaline materialsto the AMD during coal mining operations is an attempt to increase the pH and precipitate metals in the form of sludge [9].

The use of lime ($CaCO_3$, CaO) and caustic soda (NaOH) in the active management of AMD has obstacles related to their availability and negative impacts. In Jambi Province, there is no source of lime that can be mined and used to overcome the problem of AMD, so itmustbeacquiredfrom outside of the area, which of course requires additional transportation costs which are relatively expensive. In addition, NaOH compounds are chemicals containing Na, in which the continuous use can cause salinization of the land. The results of research by Endo et al. [10] showed that the use of irrigation water containing high Na (9.8 mmol/L) led to an increase in soil Na content (11.91-35.48cmol/kg) due to the accumulation of Na salts, as an indication of salinization. The use of materials such as $Ca(OH)_2$, CaO, NaOH, and $NaCO_3$ which are generally used in the management of AMD is not cost-effective because they are expensive [11,12].

Many studies have been carried out on the use of coal fly ash as a material to neutralize AMD. In their study, Gobel et al. [13] found that the addition of 5, 10, and 12 g of coal fly ash into 250 mL of AMD could increase the pH from 3.44 to 6.96, 7.94, and 7.88, respectively after 30 rpm stirring for 45 min. In addition, the study by Herlina et al. [14] foundan increasein the pH of AMD from 4.25 to 6.0 and 6.8 with the addition of 35-55 g/L of coal fly ash. However, the use of coal fly ash for the management of AMD cannot be recommended because itcontains heavy metals such as Pb, As, Ni, Ti, Cr, and V[15].

One source of substitute material that is available quite a lot to deal with AMD is ash from boilers at palm oil mills. This boiler ash is ash resulting from burning fiber along with palm fruit shells which are used as boiler fuel. Boiler ash is widely available and is a waste from boilers that have not been utilized properly and is often thrown away as a paver. Each ton of processed fresh fruit bunches produces about 4-5 kg of boiler ash [16]. Boiler ash contains 40.60% SiO_2, 19.60% CaO, and 1.35% MgO [17], which shows the characteristics of alkaline compounds that can be used to treat AMD. In their study, Hidayati and Indrayanti [18] obtained the characteristics of boiler ash with a pH of 11.82, 2.39%total Ca, and 0.47% total Mg. The large amount of boiler ash from palm oil mills with its alkaline nature indicates a huge potential for this boiler ash to be used for the improvement of AMD. The purpose of this study was to evaluate the potential of boiler ash from the palm oil mill as an alternative material for the improvement of AMD.

Materials and Methods

Laboratory Experiment

The experiment was carried out on a laboratory scale by using artificial AMD. A total of 30 liters of AMD was put into a plastic box measuring 50 cm (length) x 34 cm (width) x 34 cm (height). Then, 2.14 g $FeSO_4.7H_2O$ and 0.91 g $MnSO_4.H_2O$ were added to the AMD. This addition is intended to increase the concentration of Fe and Mn in the AMDso that it exceeds the established environmental quality standards, namely 7 mg/L total Fe and 4 mg/L total Mn (Decree of the Indonesian Minister of Environment No. 113, 2003). The experiment was carried out by taking each 500 mL sample of the AMD from a plastic box and putting it into the Erlenmeyer glasses and then adding boiler ash with a variety of dosages as shown in Table 1. Furthermore, 500 mL of AMD was taken to be treated withquicklime. Each treatment was repeated twice. Mine acid water that has been added to boiler ash and quicklime is stirred and then left for ten days.

Table 1.**Doses of boiler ash and quicklime.**

Treatment	
Boiler ash	***CaO***
mg/L	mg/L
0	0
3	0.02
6	0.03
9	0.05
12	0.1
15	0.3

Data analysis

pH, concentrations of dissolved Fe and Mn, and the precipitates of Fe and Mn from the treated AMD were subjected to regression and correlation tests to obtain the relationship between pH and concentrations of Fe and Mn in solution and their precipitates.

The measurement of pH was carried out every day for ten days by using a pH meter (Lutron pH 208). On the tenth day, 10 mL of each treated AMD solution and precipitate were taken and put into chemical tubes. Measurement of dissolved Fe and Mn content and Fe and Mn precipitate was carried out using an atomic absorption spectrophotometer (AAS) AA 6680Schimadzu, (Japan). The standard series of Fe and Mn from Merck (Germany) were used for comparison. Preparation of the samples for the calibration curve is conducted by diluting and mixing the appropriate amount of standard solution from each of the standard solutions (1000 mg/L) for a single element of Fe and Mn.

Results and Discussion

The Characteristics of Boiler Ash and Quicklime

Boiler ash has very fine physical characteristics which are very suitable for correcting pH. The materials used to neutralize the pH must be very fine to provide a large surface area and be reactive [9]. Quicklime (CaO) was used as a comparison with the fineness of passing 100mesh. The chemical composition of the boiler ash was determined using the PANalytical Epsilon 3 XRF Instrument at the Padang State University Instrument Chemistry Laboratory. The composition of boiler ash is presented in Table 2. Boiler ash contains 51.99% CaO which shows alkaline properties. As a comparison material used is quicklime or CaO contains 95% CaO. Quicklime is one of the materials that is generally used in overcoming the problem of AMD [5, 19].

Table 2. **Composition of boiler ash.**

No	Oxide	Amount (%)
1	MgO	1.47
2	SiO	25.82
3	P_2O_5	4.91
4	K_2O	10.39
5	CaO	51.99
6	Fe_2O_3	3.84
7	MnO	0.21

pH value of AMD after the treatment of boiler ash and quicklime

The addition of boiler ash and CaO increased the pH of AMD (Table 3 and Table 4). The pH of AMD increased with the increasing doses of boiler ash and CaO given. The pH of AMD in the control experienced very small changes and was relatively stable for ten days, namely 3.37-3.45. By adding boiler ash and CaO, the pH value tended to increase from day one to the fourth and fifth. The pH showed decreases from the sixth to the tenth day. The addition of 3, 6, 9, 12, and 15 mg/L of boiler ash increased the pH value to 7.21, 7.56, 8.23, and 8.65, respectively on the first day and increased to 7.91, 8.41, 8.81, 9.31, and 9.58, respectively on the tenth day. The pH values in the treatments of 3, 6, and 9 mg/L boiler ash on the tenth day still met the environmental quality standards for AMD namely 6-9. In contrast, the treatments of 12 and 15 mg/L boiler ash increased the pH to 9.31 and 9.38, respectively on the tenth day, in which this value was higher than the quality standard, which was 6-9. The ability of boiler ash to increase pH is due to the CaO content of 51.99% of boiler ash which shows its alkalinity as illustrated inTable2.The study by Petrilakova et al. [23] found that the increase in the pH of the AMD solution with the addition of coal fly ash was due to the role of the CaO content. An increase in pH causes the removal of metals from the solution and forms precipitates [24]. The increase in the pH of AMD occurs with the addition of alkaline materials, in which the increasing pH is related to the increasing concentration of alkaline [25].

The addition of 0.02, 003, 005, 01, and 0.3 mg/L CaO increased the pH of acid mine water to 6.75, 7.12, 9.27 10.73, and 11.69, respectively on the first day. On the fifth day, there was generally a decrease, and on the tenth day, the AMD pH values were 7.76, 7.80, 8.08, 8.96, and 11.06 for treatments 0.02, 03, 05, 0.1, and 0. 3 mg/L CaO. The pH value of 11.06 exceeds the quality standard, namely pH 6-9, while the pH values of 7.76, 7.80, 8.08, and 8.96 meet environmental quality standards. These showed that the addition of CaO at a dose of more than or equal to 0.05 mg/L gave high pH values initially, but they decreased in the following days. The decrease in pH values is thought to be becausethe AMD had been saturated with CaO and some of the CaO did not dissolve inwater and precipitates over time. CaO is one of the alkaline materials that is oftenused to overcome the acidity of AMD besides $CaCO_3$ and NaOH. The CaOhas a neutralization efficiency of 90%. However, it is six times more expensive than $CaCO_3$ [4]. Alkaline materials such as boiler ash and quicklime improve the pH of AMD, although boiler ash requires a higher concentration in raising the pH of AMD compared to quicklime. Alkaline-rich materials create alkaline conditions in the water [26].

***Table 3*.pH of AMD after the treatment of boiler ash.**

Boiler ash (mg/L)	Time (Days)									
	1	2	3	4	5	6	7	8	9	10
	pH									
0	3.37	3.42	3.39	3.38	3.38	3.42	3.45	3.43	3.44	3.45
3	6.16	7.59	7.88	8.11	8.12	8.11	8.08	8.02	7.96	7.91
6	7.21	8.31	8.58	8.72	8.71	8.67	8.52	8.48	8.42	8.41
9	7.56	8.81	9.17	9.25	9.25	9.21	9.16	9.14	9.12	8.81
12	8.23	9.07	9.39	9.43	9.45	9.41	9.36	9.34	9.32	9.31
15	8.65	9.26	9.63	9.64	9.68	9.65	9.62	9.57	9.59	9.58

Table 4.**pH of AMD after the treatment of quicklime (CaO).**

CaO (mg/L)	Time (Days)									
	1	2	3	4	5	6	7	8	9	10
	pH									
0	3.37	3.42	3.39	3.38	3.38	3.42	3.45	3.43	3.44	3.45
0.02	6.75	7.58	7.83	7.86	7.84	7.84	7.82	7.81	7.79	7.76
0.03	7.12	7.64	7.87	7.90	7.90	7.87	7.85	7.83	7.81	7.80
0.05	9.27	8.25	8.10	8.16	8.19	8.16	8.15	8.11	8.09	8.08
0.1	10.73	10.03	9.65	9.56	9.37	9.15	9.11	8.99	8.98	8.96
0.3	11.69	11.72	11.59	11.58	11.44	11.38	11.22	11.23	11.09	11.06

The concentrations of Fe and Mn in AMD after the addition of boiler ash and quicklime

The concentrations of dissolved Fe and Mn in the AMD decreased after the addition of boiler ash as shown in Table 5 and CaO as illustrated in Table 6. The concentrations of dissolved Fe and Mn becamelower with higher doses of boiler ash and CaO given. The concentrations of dissolved Fe and Mn without boiler ash and CaO treatment were 3.122 and 2.266 mg/L, respectively, whereas the boiler ash treatment of 15 mg/L resulted inthe lowest decrease of Fe and Mn, namely 1.063 mg/L, and 0.953 mg/L, respectively. The lowest concentrations ofdissolved Fe and Mn in the AMD 1.025, and 0.931 mg/L, respectively were obtained with thetreatment of 0.3 mg/L CaO. In contrast, the precipitates of Fe and Mn in the AMD increased with increasing doses of boiler ash as illustrated in Table 5and CaOas shown in Table 6. The highest Fe and Mn precipitates were 16.951, and 10.243 mg/L, respectively occurred with the addition of 15 mg/L of boiler ash, while the addition of 0.3 mg/L CaO gave the highest Fe and Mn precipitates of 9.056 and 9.164 mg/L, respectively.

The addition of boiler ash and quicklime increased the pH of AMD, decreased the Fe and Mn content of AMD, and increased the content of Fe and Mn precipitates. In the boiler ash treatment, theFe content of the precipitate was higher than in the quicklime treatment.

Table 5.**The concentrations of dissolved Fe and Mn, and their precipitates in AMD after the addition of boilerash**.

Treatment	AMD			
Boiler ash mg/L	Dissolved		Precipitate	
	Fe	*Mn*	*Fe*	*Mn*
	mg/L		mg/L	
0	3.122	2.266	8.746	7.837
3	2.816	1.056	10.922	7.592
6	2.042	1.210	12.798	7.927
9	2.311	1.031	14.603	8.530
12	1.702	0.908	15.109	8.227
15	1.063	0.953	16.951	10.243

Table 6.**The concentrations of dissolved Fe and Mn, and their precipitates in AMD after the addition of quicklime (CaO)**.

Treatment	AMD			
	Dissolved		Precipitate	
CaO mg/L	*Fe*	*Mn*	*Fe*	*Mn*
	mg/L		mg/L	
0	3.122	2.266	8.746	7.837
0.02	1.495	1.637	7.939	8.908
0.03	1.297	1.569	8.149	9.320
0.05	1.234	1.525	8.980	9.546
0.10	1.178	1.348	9.178	9.502
0.30	1.025	0.931	9.056	9.614

This could originate from the Fe contained in boiler ash because it contains 3.84% Fe_2O_3as shown in Table 2. The addition of alkaline materials can neutralize the AMD and precipitate sulfuric acid (H_2SO_4) contained in the AMD into gypsum ($CaSO_4$. $2H_2O$), and sulfuric acid becomes unreactive on the surface [26]. The increase in the pH of AMD with the addition of alkaline materials such as boiler ash and quicklime is due to the supply of hydroxide ions (OH) so that Fe and Mn metals dissolved in water form Fe and Mn hydroxides which are insoluble and precipitate [26]. In AMD, under anaerobic conditions, Fe is mainly present in the ferrous form, and it is necessary to increase the pH of the solution to ≥ 8.5 to form ferrous hydroxide precipitates, and in general other metals precipitate in the pH range 6-9 [4].

The pH value showed a negative correlation with the dissolved Fe concentration in AMDwith the boiler ash treatment (R^2=0.620). Fig 1.shows thatthe increasing pH resulted inthe decreasing trend of the dissolved Fe. A significant negative correlation was found between pH and dissolved Mn concentration with the boiler ash treatment (R^2 = 0.963). The results (Fig. 1 and Fig. 2) show that a significant negative correlation was also found between the values of pH, and the dissolved Fe and Mn with the quicklime treatment (R^2=0.871; 0.989).

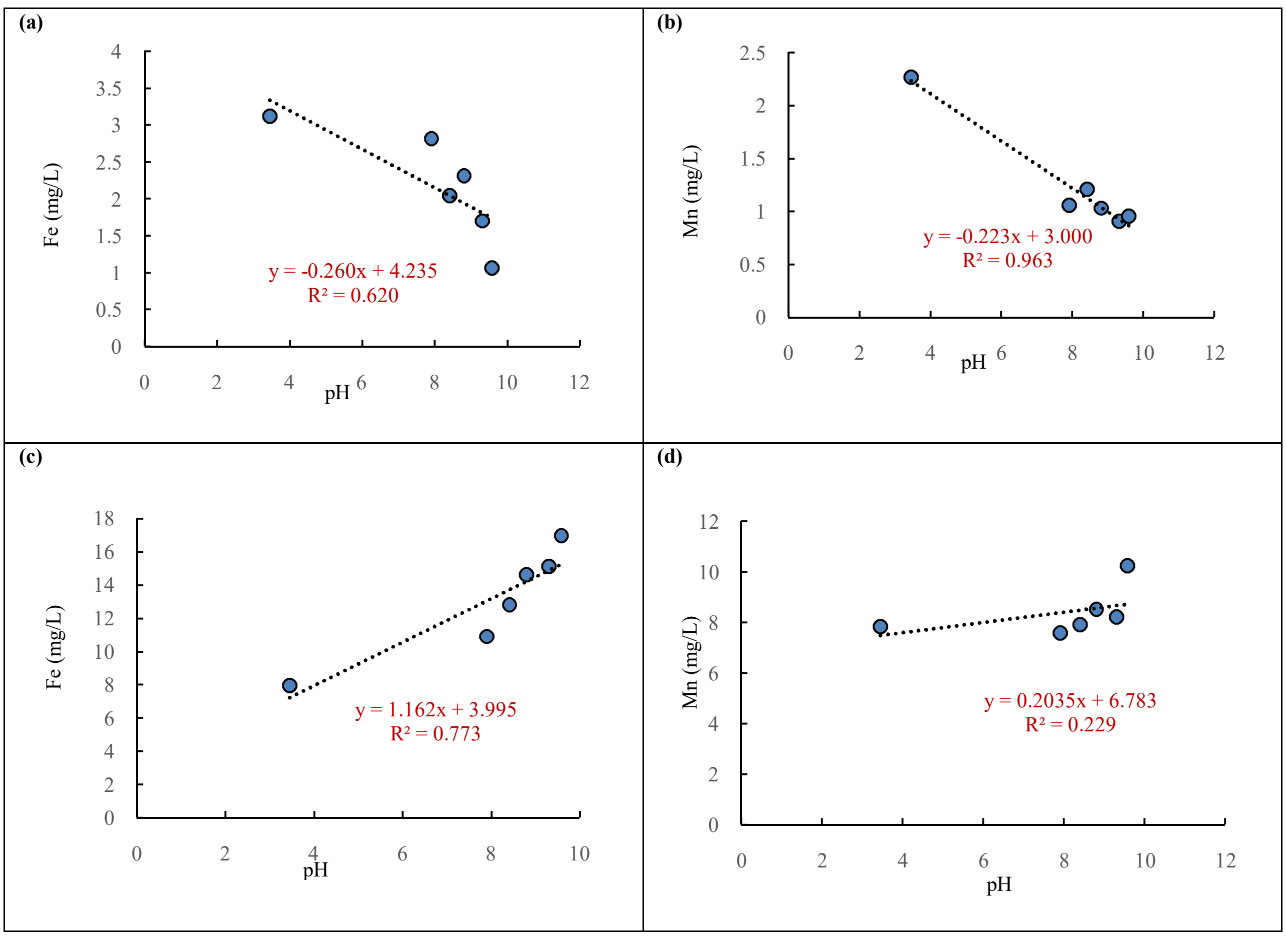

***Figure 1*. Correlation between pH and the concentration of dissolved Fe (a) and Mn (b), and the precipitates of Fe (c) and Mn (d) due to the boiler ash treatment**

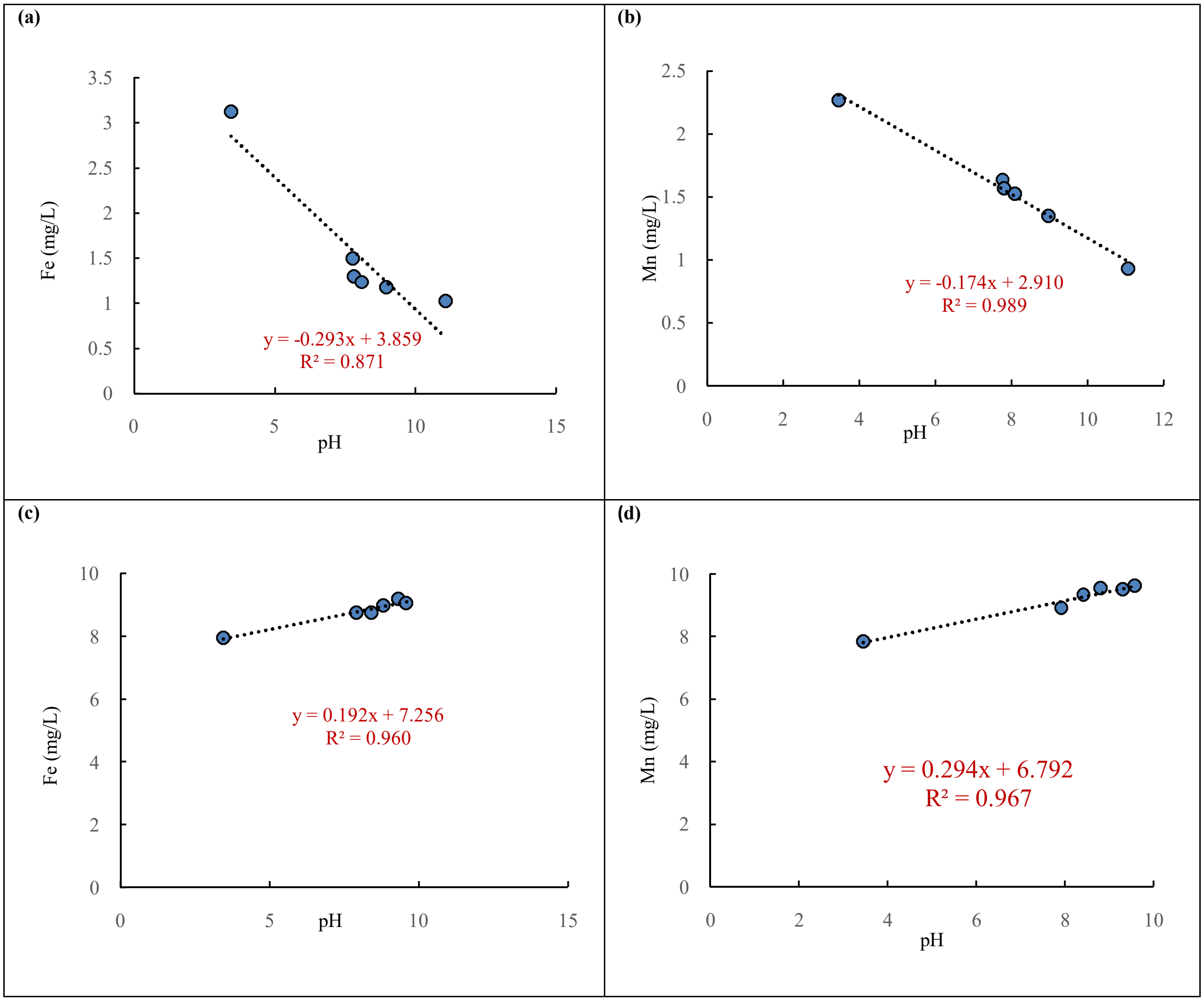

Figure 2. **Correlation between pH and the concentration of dissolved Fe (a) and Mn (b), and the precipitates of Fe (c) and Mn (d) due to the quicklime treatment**

The increase in pH due to the addition of boiler ash and quicklime causes a decrease in the concentration of dissolved Fe and Mn in the AMD. The pH value did not significantly correlate positively with Fe and Mn precipitates in the boiler ash treatment (R^2=0.773; 0.229 Fig. 1). However, with the boiler ash treatment, as the pH increased, the Fe and Mn precipitates also tended to increase. With the quicklime treatment, pH had a significant positive correlationwith the concentration of Fe and Mn precipitates (R^2 = 0.960;0.967) as shown inFig. 2 which showed the increasing pH caused theincreasing concentration of Fe and Mn precipitates.

The addition of boiler ash and quicklime increased pH(Table 3 and Table 4), decreased the concentration of dissolved Fe and Mn,and increased the concentration of Fe and Mn precipitates(Table 5 and Table 6). The higher the pH, the more Fe and Mn precipitate with the treatment of boiler ash and quicklime. The pH value determines the concentration ofdissolved Fe and Mn and the concentration ofprecipitates of Fe and Mn. These results are consistent with Bortnikovaet al. [6], who found that the concentrations of the precipitates ofFe and Mn in AMD changed with an increase in pH, whereas the precipitates of Fe and Mn increased with an increase in pH. If the concentration of Fe in water is much greater than the Mn content, a solution of pH ≥ 9 is required to precipitate Mn and sometimes a pH of 10.5 is needed to precipitate Mn [4]. Increasing the pH of water to a certainlevel is related to the precipitation of metals in the hydroxide form [25]. With the formation of precipitates, the mobility of metals and the level of toxicity in solution decreases [26].

Conclusion

The addition of boiler ash and quicklime increased the pH and decreased the concentration of dissolved Fe and Mn and increased the precipitates of Fe and Mn in the AMD. The increasing doses of boiler ash and quicklime applied to AMD showed an increasing trend of pH, a decreasing trend of dissolved Fe and Mn, and an increasing trend of Fe and Mn precipitates.The increasing pH of AMD with the addition of boiler ash and quicklime was followed by the decreasing concentration of dissolved Fe and Mn and the increasing concentration of Fe and Mn precipitates. The highest pH value, the lowest concentration of Fe and Mn and the highest precipitates of Fe and Mn were obtained by treatingAMD with 15 mg/L ofboiler ash and 0.3 mg/L quicklime, respectively.The capacity of boiler ash to improve AMD indicates its promise as an alternative and inexpensive material, even though more boiler ash is needed than quicklime.

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Conflict of Interest

The authors declare no conflict of interest.

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