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Chemical characteristics of organic wastes and their potential use for acid mine drainage remediation

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ABSTRACT

Organic substrate is an important component of biological treatments for acid mine drainage (AMD) remediation systems. It provides organic substrates to sulfate-reducing bacteria (SRB) in the sulfate (SO4) reduction, resulting in increased alkalinity and metal sulfide precipitates. Natural organic matters vary in their characteristics, and therefore may perform differently for remediation properties. This study was aimed to characterize four locally available organic wastes (bark, empty fruit bunch, sawdust, and chicken manure) potential for AMD remediation. Their chemical properties and elemental compositions were measured. An anaerobic incubation of these wastes in AMD was undertaken to determine their remediation properties. The pH, electrical conductivity (EC), redox potential (Eh), and dissolved Fe and SO_4 of the mixtures were measured after the 1st, 7th, 14th, and 30th day of the incubation at room temperature. The results demonstrated that organic wastes varied in their chemical properties and performed differently in treating AMD. Organic wastes containing high alkalinity (high pH) and nutrient concentrations (chicken manure and empty fruit bunch) improved AMD quality through increasing pH (>6) and reducing dissolved Fe and SO4 concentrations. Although sawdust and bark (high CEC) did not increase pH up to acceptable standard at most time, they apparently were able to remove dissolved Fe from AMD through adsorption mechanism.

Keywords: acid mine drainage, anaerobic incubation, organic wastes, remediation.

INTRODUCTION

Acid mine drainage (AMD) is one of most serious problems facing mine industries worldwide, including coal industry in Indonesia. This is due to its high acidity (pH can be as low as 2) and elevated concentrations of dissolved metals and sulfates which are potentially hazardous to the environment, especially aquatic systems Therefore it should be treated before being discharged to water.

A number of techniques have been developed to reduce acidity and dissolved metals and sulfate concentrations. A promising and increasingly accepted method is biological treatment systems, such as constructed wetlands and bioreactors. These biological approaches involve the use of organic materials and anaerobic sulfate-reducing bacteria (SRB) which reduce sulfate to sulfide by oxidizing the organic carbon source (Gibert *et al*., 2004; Liamleam & Annachhatre 2007). The sulfate reduction into sulfide is described in the following reaction:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2\,HCO_3^-,$$

CH_2O represents a simple organic carbon (C). Sulfate reduction reactions consume SO_4^{2-}, produce H_2S, and result in increased alkalinity and pH. The released bicarbonate neutralizes the acidity, increases the alkalinity of AMD, and enhances precipitation of metal carbonates minerals. In the presence of metal ions, as generally found in AMD, the released H_2S will react to form insoluble metal sulfides, removing sufates from the water (Drury 1999; Luptakova & Kusnierova 2005; Machemer & Wildeman 1992; Song *et al*., 2001; Zagury *et al*., 2006). A reaction between sulfides and metal ions can be described as follows:

$$Me^{2+} + S^{2-} \rightarrow MeS$$

where Me^{2+} represents cationic metals, such as lead (Pb), (cobalt) Co, cadmium (Cd), copper (Cu), nickel (Ni), iron (Fe), and zinc (Zn) (Drury 1999; Zagury *et al*., 2006).

Acid mine drainage generally contains relatively low concentrations of dissolved organic C (<10 mg/l)

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(Kolmert & Johnson 2001). Therefore, availability of C from an additional organic source is the most critical limiting factor for microbial activity (Gibert *et al*., 2004; Zagury *et al*., 2006). Various types of organic substances have been studied as electron donors and C sources including sewage sludge, leaf mulch, wood chips, animal manure, vegetal compost, sawdust, mushroom compost, whey, and other agricultural waste (Waybrant *et al*., 1998). Due to their wide ranges of characteristics, they can result in different effectiveness in treating AMD. Chemical characteristics such as ratio of organic carbon and total nitrogen (C/N), availability of low-molecular weight compounds (Liamleam & Annachhatre 2007), and adsorption sites have been identified to be responsible for remediation effects. High electrical conductivity (EC) has been found to have a strong correlation with high adsorption sites of the substrates (Gibert *et al*., 2004). Based on these, it is therefore, selection of suitable organic substrates for passive treatments is very important.

This laboratory study was aimed to characterize locally-available organic wastes (empty fruit bunch, bark, chicken manure, and sawdust) and explore their potential use for acid mine drainage remediation. It is roughly estimated that more than 20 million tons of empty fruit bunch is produced by palm oil industry in Indonesia and tend to increase annually (Isrori 2008). Bark is one of main solid wastes of pulp and paper industries (Purwati *et al*., 2007), chicken manure is produced by livestock industries and traditional farmers and commonly used as fertilizer in agriculture, while sawdust is produced by sawmills industry commonly found in surrounding areas of mine sites.

MATERIALS AND METHODS

This laboratory experiment was conducted in Soil Science Laboratory, the Department of Agronomy, University of Bengkulu, Bengkulu, Indonesia from March to November 2007.

Four different organic wastes were used in this study: bark of tree stem (BK), empty fruit buch of palm oil (EFB), sawdust (SD), and chicken manure (CM). The bark was supplied by a pulp and paper industry of Tanjung Enim Lestari Co., South Sumatra. Empty fruit bunch was collected from a crump palm oil (CPO) industry Bio Nusantara Co., Bengkulu, and the sawdust was obtained from a local sawmill industry in Bengkulu. Chicken manure was obtained from a local farm in Bengkulu. All these four organic waste materials were considered to be potentially suitable organic materials with respect to their availability. The acid mine drainage (AMD) was collected from Banko Barat Mine Unit of PT Tambang Batubara Bukit Asam (PERSERO) Tbk, Tanjung Enim, South Sumatra.

Characterization of Organic Wastes and Acid Mine Drainage. All organic waste materials were air-dried, and to obtain uniform size they were manually cut into 2-5 cm size, and passed through a 5 cm-diameter sieve. They were brought to Soil Science Laboratory, Faculty of Agriculture, University of Bengkulu for analyses of total organic carbon (C), total nitrogen (N), total phosphorus (P), total cations (Ca, Mg, Na, Mn, Fe, and Zn), cation exchange capacity (CEC), electrical conductivity (EC), and pH(H_2O) (Balai Penelitian Tanah 2005).

The chemical characterisations of AMD included measurements of pH and redox potential (Eh) and EC using electronic pH-meter, lithium-electrode provided pH/mV-meter, and electrical conductivity-meter, respectively. Whereas concentrations of dissolved cations (Ca, Mg, Al, Fe, and Mn) and sulfate (SO4) analyses were determined using an Atomic Absorption Spectrophotometer and UV-Vis Spectrophotometer, respectively (Balai Penelitian Tanah 2005).

Remediation Effects of Organic Wastes on AMD Quality. An anaerobic bach experiment was conducted to test remediative effects of organic wastes to AMD. All individual organic wastes were weighed to obtain 250 g and put in the 2-L plastic containers and added with 1250 ml AMD, with three replications. Organic materials were well mixed with AMD and containers were covered and allowed to anaerobically incubate at room temperature. A set of 4 extra containers containing same mixtures were prepared for destructive AMD samplings. During the experiment, pH, redox potential (Eh), and EC of the mixtures were measured after the 1st, 7th, 14th, and 30th days of incubation. The AMD samples were taken from the extra containers for analyses of dissolved iron (Fe) and sulphates (SO^2_4) concentrations. All measurement methods used in AMD characterization were also employed in this experiment.

RESULTS AND DISCUSSIONS

Organic Waste and AMD Characteristics, Organic wastes used in this experiment varied in their chemical properties and elemental compositions as shown in Table 1. Sawdust and bark were acidic with pH of 4.90 and 5.50 respectively, whereas the chicken

Table 1. Chemical properties and elemental composition of the organic wastes.

Chemical properties:	Organic wastes			
	Bark (BK)	Chicken Manure (CM)	Empty Fruit Bunch (EFB)	Sawdust (SD)
pH	5.50	7.80	6.70	4.90
EC, µS cm^{-1}	365	1645	2700	70
CEC, cmole kg^{-1}	29.79	18.29	13.80	31.59
Elemental composition:				
Total C, %	43.58	20.02	54.29	55.83
Total N, %	0.22	0.95	0.40	0.69
C/N	198.09	21.09	135.72	80.91
Total P, %	0.23	2.16	0.37	0.27
Total K, %	0.24	1.02	1.19	0.06
Total Ca, %	0.58	0.72	0.15	0.18
Total Mg, %	0.16	0.74	0.64	0.08
Total Na, %	0.17	0.53	0.65	0.14
Total Fe, mg L^{-1}	3500	13600	700	1800
Total Mn, mg L^{-1}	117.07	417.22	53.27	4.79
Total Zn, mg L^{-1}	6.88	283.36	77.43	42.05

Table 2. Chemical properties of the AMD used in the study

Properties	Unit	Values
pH	-	2.50
Electrical conductivity (EC)	µS cm^{-1}	1394.00
Reduction-oxidation potential (Eh)	mV	769.00
Total dissolved calcium (Ca)	mg L^{-1}	33.73
Total dissolved magnesium(Mg)	mg L^{-1}	83.31
Total dissolved aluminium (Al)	mg L^{-1}	7.36
Total dissolved iron (Fe)	mg L^{-1}	7.78
Total dissolved manganese (Mn)	mg L^{-1}	3.54
Total dissolved sulfate (SO4)	mg L^{-1}	407.28

manure and empty fruit bunch tended to be alkaline with their respective pH of 7.80 and 6.70. Elemental analyses found that the alkaline organic wastes generally contained higher macronutrients (P, K, Ca, and Mg) and some micronutrients compared to the acidic organic wastes. Organic wastes with higher pH and basic cations (K, Ca, Mg, and Na) had likely become potential sources of alkalinity for AMD treatments. As expected, higher nutrient element concentrations corresponded with higher EC values. Gibert *et al.,* (2004) found that biodegradable substrates (poultry and sheep manures) more effective in removing SO^4 from AMD than recalcitrant substrates, such as oak leaf. However, this study also demonstrated that although having lower degradability, bark and sawdust were able to improve AMD. Their higher cation exchange capacity (CEC) indicated that these substrates were able to retain higher amount of cations, such as potentially-hazardous metals contained on the exchange sites, removing the dissolved cations in the AMD.

Nutrient analyses also revealed that total organic C was lower in chicken manure (20.02%) compared to the other organic wastes ranging between 43% and 60%. On the other hand, the chicken manure contained highest total N content (0.95%). These variations resulted in wide ranges of C/N ratios of the organic wates, between 21 and 200. The chicken manure had lowest C/N ratio (21.09), whereas wood bark had highest (198.09). Earlier studies by Gibert *et al.,* (2004) reported that a maximum C/N ratio for sulfate-reducing bacteria (SRB) was in the range of 45-120. Lower C/N ratio may suggest a lack of C, whereas higher ratios indicate excessive C or N deficiency. Therefore, although chicken manure was highest in alkalinity and nutrient elements, it might not sufficiently provide C for long-term support for SRB in reducing SO^4. On the other hand, organic wastes with very high C/N ratios such as bark and empty fruit bunch might have sufficient C, but they are not easily degradable due to possible high lignin content. Therefore, Liamleam and Annachhatre (2007) recommended that a preferred organic electron donor and C source consist of more than one type of electron donors to obtain best performance of SO^4 reduction by SRB. Mixtures containing multiple organic substances have been reported to be higher in sulfate reducing rates compared with those containing a single organic substrate (Waybrant *et al*., 1998).

Data in Table. 2 show that acid mine drainage (AMD) used in this experiment was very acidic (pH 2.5), high dissolved oxygen (high positive Eh) and EC, low in dissolved basic cations (Ca and Mg), moderate to fairly high dissolved acidic cations (Al, Fe, and Mn) and sulfate (SO^4) concentrations. These characteristics suggest that treatment methods for this AMD should involve additions of alkaline materials and materials which are able to create reducing conditions for removing potentially-hazardous metals and SO^4. The following section discusses the changes of AMD properties as affected by additions of the organic wastes under anaerobic condition.

Remediative Effects of Organic Wastes in Anaerobic Incubation. All organic wastes significantly increased pH of the AMD (Figure 1a) from its original pH (2.5). However, the increments varied among the organic materials over the entire experiment, depending on their properties. The increment in pH of AMD well correlated with original pH of the organic wastes. During the experiment chicken manure-AMD mixture had constantly highest pH (>7), followed by empty fruit bunch (pH>6). On the contrary, the pH of sawdust-AMD mixture was constantly lower than acceptable pH value (6). High contents of basic cations such as Ca, Mg, and Na in the chicken manure and empty fruit bunch apparently correlated with the increase in pH of AMD. Higher concentrations of nutrient elements in these organic materials and by high EC (Figure 1b) might have enhanced biological activity, resulting in high oxygen consumption which then created reduced conditions (Eh more negative) during the entire incubation (Figure 1c) and consequently increased alkalinity. Gibert *et al*., (2004) found that the lower the content of lignin in the organic substrate such as sheep manure, the higher its biodegradability and capacity for developing bacterial activity. Such reactions demand oxygen due to increasing metabolic process (Cunha-Santino & Bianchini 2006), such as re-oxidation of anaerobic respiration (Hansen & Blackburn 1991). Although not as much reduction as in the chicken manure- and empty fruit bunch-AMD mixtures, additions of the other two organic wastes had also significantly decreased Eh, particularly after the second week of incubation.

In general additions of organic wastes had significantly decreased dissolved Fe concentrations in AMD as shown in Figure 2a. Decrease in the dissolved Fe was greater under sawdust and bark-AMD mixtures compared with that under chicken manure- and empty fruit bunch-AMD mixtures, although the later had more reduced conditions. This unexpected phenomenon

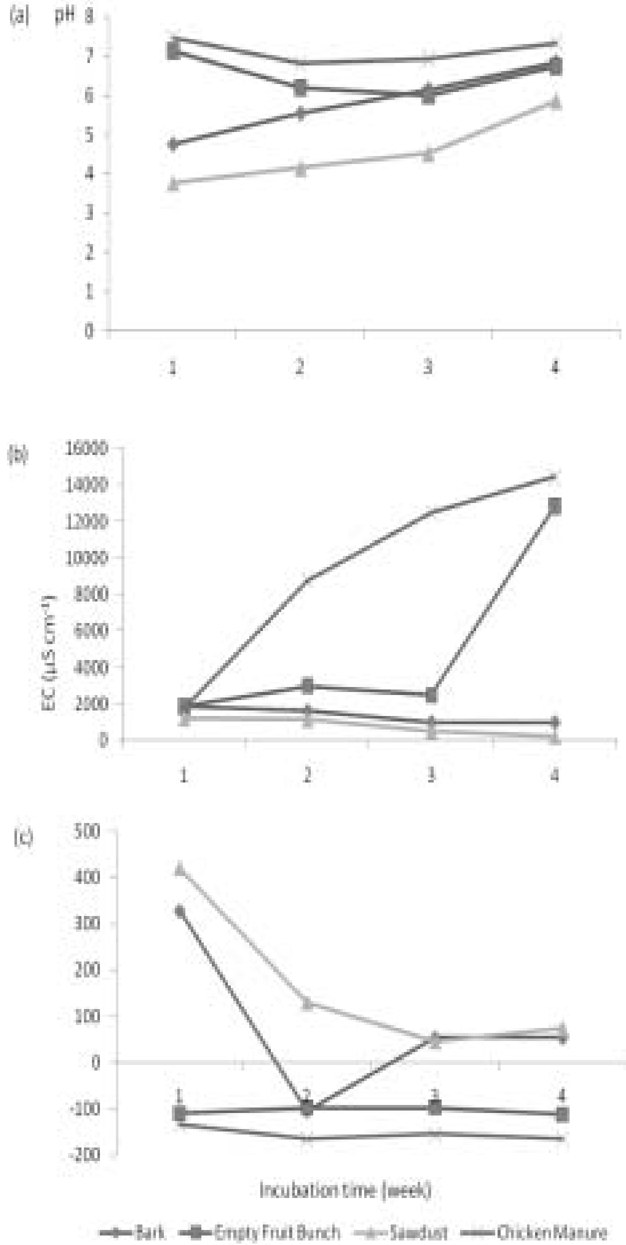

Figure 1. Changes in (a) pH, (b) electrical conductivity (EC), and (C) redox potential (Eh) of the AMD as affected by organic wastes additions during the incubation time

could clearly be explained by Figure 2b. Figure 2b shows that the initial reducing condition (decline in Eh) developed in the first two weeks (between -100 and -200 mV) in the chicken manure- and empty fruit bunch-AMD mixtures was not sufficiently able to reduce significant amounts of SO^4 to form Fe-sulfides. Reduction of SO^4 apparently occurred later after the third week of incubation. Based on this fact, the decrease in Fe concentrations (Figure 2a) compared to the original AMD (7.78 mg l^{-1}) in the first two week was not due to precipitation of Fe-sulfide, but more likely due to Fe retention to organic matter. The sawdust and bark materials, which had higher CEC as shown in Table

1, were able to retain more Fe, resulting in lower dissolved Fe concentrations (Figure 2a). Zagury *et al*., (2006) explained that metal removal tends to occur earlier compared with SO^4 reduction, through adsorption of the metals onto organic matter. Once reduced conditions are established, sulfide metal precipitation becomes predominant mechanism of the metal removal from AMD (Song *et al*., 2001; Zagury *et al*., 2006), resulting in alkalinity production.

Sulfate reduction into metal-sulfides such as Fe- and Zn-sulfides might have occurred in the third week, as indicated by declining SO4 concentration (Figure 2b). Higher SO4 concentration in the chicken manure-AMD mixture was probably due to released SO4 salts over incubation period, yielding high EC (Figure 1c). Although SO^4 concentration was not further measured after third week, given trends of the curves, reducing condition would likely take place further beyond this period. Therefore, if metals such as Fe and Zn were adequately available, formation of metal-sulfides would occur. Good performance of manure for AMD remediation has been reported in a number of studies elsewhere. Gibert *et al*., (2004) observed that seep manure was successful for creating reduced condition and sustaining sulfide generations by removing 99% SO^4.

The complex organic C source (sawdust) did not perform well compared to other organic wastes in AMD remediation. Although higher than original values, the pH of sawdust-AMD mixture was constantly lower than the acceptable value (pH 6). Sawdust has been considered as recalcitrant compound or cellulosic waste (Neculita *et al*., 2007); therefore, it did not easily react with AMD. Marschner and Kalbitz (2003) found that the recalcitrant fraction remains in the solution up to 180 days of incubation. Low EC and nutrient concentrations of the sawdust (Table 1) were likely unfavourable for microbial activity, as indicated by relatively constant and high (positive) Eh values during the experiment. Similar data were also reported by other investigators (Cocos *et al*., 2002; Figueroa *et al*., 2004; and Zagury *et al*., 2005). They suggested, therefore, that balanced mixtures of organic materials containing high organic acid and saccharide fractions quickly consumed by sulphate-reducing bacteria (SRB) such as manures, with more recalcitrant compounds (lignocelluloses) such as sawdust and wood chips result in sustained SRB. Therefore, although sawdust and other similar materials do not individually remediate AMD, additions of these materials into fertile organic wastes like chicken manure is necessary to provide long-term C source for SRB and favorable physical properties of the organic matter for AMD treatment (Cocos *et al*., 2002). Zagury *et al*., (2007) stated that the most efficient mixtures usually contain relatively easily biodegradable sources, such as manure and sludge, and recalcitrant ones, such as sawdust and wood chips.

CONCLUSIONS

Organic wastes varied in their properties and performed differently in treating AMD. Organic wastes containing high alkalinity (high pH) and nutrient concentrations (chicken manure and empty fruit bunch) improved AMD quality through increasing pH (>6) and reducing Fe and SO^4 concentrations. Although sawdust and bark did not significantly increase pH up to acceptable standard, they apparently were able to remove dissolved Fe from AMD possibly through adsorption mechanism. In summary, all these organic wastes are potential for biological treatments of AMD.

Based on the results of this study and results from other investigators described above, it is necessary to further study on quantitative measures of detailed compositions of the organic wastes and their appropriate mixtures used for anaerobic treatment systems which rely on sulfate-reducing mechanism by SRB.

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