Journal of Environmental Management 177 (2016) 153–160

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Vegetation successfully prevents oxidization of sulfide minerals in mine tailings

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ARTICLE INFO

Article history:
Received 2 November 2015
Received in revised form
9 April 2016
Accepted 9 April 2016

Keywords:
Sulfur oxidization
Mine tailings
Chemical oxidization
Biological oxidization

ABSTRACT

The oxidization of metal sulfide in tailings causes acid mine drainage. However, it remains unclear whether vegetation prevents the oxidization of metal sulfides. The oxidization characteristics and microbial indices of the tailings in the presence of various plant species were investigated to explore the effects of vegetation on the oxidization of sulfide minerals in tailings. The pH, reducing sulfur, free iron oxides (Fe_d), chemical oxygen consumption (COC) and biological oxygen consumption (BOC) were measured. Key iron- and sulfur-oxidizing bacteria (*Acidithiobacillus* spp., *Leptospirillum* spp. and *Thiobacillus* spp.) were quantified using real-time PCR. The results indicate that vegetation growing on tailings can effectively prevent the oxidization of sulfide minerals in tailings. A higher pH and reducing-sulfur content and lower Fe_d were observed in the 0–30 cm depth interval in the presence of vegetation compared to bare tailings (BT). The COC gradually decreased with depth in all of the soil profiles; specifically, the COC rapidly decreased in the 10–20 cm interval in the presence of vegetation but gradually decreased in the BT profiles. *Imperata cylindrica* (IC) and *Chrysopogon zizanoides* (CZ) profiles contained the highest BOC in the 10–20 cm interval. The abundance of key iron- and sulfur-oxidizing bacteria in the vegetated tailings were significantly lower than in the BT; in particular, IC was associated with the lowest iron- and sulfur-oxidizing bacterial abundance. In conclusion, vegetation successfully prevented the oxidization of sulfide minerals in the tailings, and *Imperata cylindrica* is the most effective in reducing the number of iron- and sulfur-oxidizing bacteria and helped to prevent the oxidization of sulfide minerals in the long term.

1. Introduction

Copper mine tailings resulting from mineral separation contain small amounts of sulfide minerals including pyrite/marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), gelenite (PbS), pentlandite ($((Fe,Ni_9)S_8)$), and arsenopyrite (FeAsS). The oxidization of sulfide minerals takes place in three pivotal steps. In the case of pyrite, these steps are oxidization of sulfur (Eq. (1)), oxidization of ferrous iron (Eq. (2)), and hydrolysis and precipitation of ferric complexes and minerals (Eq. (3)) (Dold, 2014).

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

The exposure of sulfide minerals to the atmosphere in the presence of water (Elberling et al., 2000; Schrenk et al., 1998) causes the oxidization of pyrite and the production of sulfuric acid. Fe^{2+} released by sulfide oxidization via Eq. (1) may be further oxidized, hydrolyzed, and precipitated as amorphous or crystalline ferric oxyhydroxide (Eq. (4)) (Blowes et al., 1998; Martín et al., 2008).

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+ \quad (4)$$

The oxidization of pyrite is controlled by chemical factors (oxygen and water content), and this oxidization rate is relatively slow. With decreasing pH, acidophiles, which are closely related to

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http://dx.doi.org/10.1016/j.jenvman.2016.04.026
0301-4797/

cultured bacteria capable of iron and sulfur oxidization/reduction and carbon oxidization/fixation (Mendez et al., 2008), particularly *Acidithiobacillus* spp. and *Leptospirillum* spp., gradually become the dominant microbial communities in tailings. These acidophiles obtain energy by oxidizing ferrous iron to ferric iron, which increases the oxidization rate of ferrous iron (Dold, 2014). In low-pH conditions, ferric iron is the main oxidant used by microorganisms to catalyze the sulfide oxidization and to generate abundant protons and sulfate (Diaby et al., 2007). Therefore, these bacteria have been thought to play a vital role in increasing the rate of acid generation, and the inhibition of bacterial activity can retard the rate of acid generation (Akcil and Koldas, 2006; Chen et al., 2014; Korehi et al., 2013). The oxidization of sulfide minerals increases the amount of free iron oxides (including amorphous and crystalline ferric oxyhydroxide) and decreases the pH and reduced sulfur via processes that are controlled primarily by oxygen, the water content and microorganisms.

Vegetation is often promoted on mine tailings because it can effectively control the erosion of tailings fines by wind and water and can improve the landscape of tailings wastelands (Mendez and Maier, 2008). However, once the oxidization of sulfide minerals in tailings is triggered, it is difficult to successfully establish vegetation, and even established vegetation is subject to degeneration or loss (Mudd and Patterson, 2010). Recent studies revealed that vegetation directly affects the structure and diversity of microbial communities in tailings (Li et al., 2014; Solís-Dominguez et al., 2012) and improves the hydrothermal conditions in tailings (Kabas et al., 2012; Naeth et al., 2011); thus, vegetation has also been regarded as being capable of controlling the oxidization of sulfur minerals. However, whether vegetation can effectively prevent the oxidization of sulfide minerals in tailings is still under debate.

Tongling is an area important for the mining of non-ferrous metals in China. A large amount of copper mine tailings is stacked in several tailings ponds. Field investigations found that a number of native plant communities have been established in the tailings ponds, including *Imperata cylindrica*, *Cynodon dactylon*, *Equisetum hyemale*, *Zoysia sinica*, *Miscanthus floridulus*, and *Rhus chinensis* (Shen et al., 2014; Zhan and Sun, 2014). In addition, some other artificial cultivated plants were found, such as *Chrysopogon zizanoides* and *Cynodon dactylon*, were widely used in ecological restoration of the mine tailings in the study district. The oxidization characteristics and microbial indices of the tailings in the presence of various plant species were investigated in this study. The primary goals were (1) to explore the effects of vegetation on the oxidization of sulfide minerals in tailings and (2) to identify suitable plant species for controlling sulfide oxidation in mine tailings.

2. Materials and methods

2.1. Field investigation

The Shuimuchong tailings pond (30°55′N, 117°50′E), which was built in 1990 and measures 44 ha, is located in Tongling City, Anhui Province, eastern China. The average annual rainfall in this area is 1346 mm, and the rainy season spans from May to September. The average annual temperature is 16.2 °C. The frost-free period spans 237–258 days. Natural *Imperata cylindrica* (IC) and *Rhus chinensis* (RC) and artificial *Chrysopogon zizanoides* (CZ) were established and growing well in the eastern area of this tailings pond. The western area of this tailings pond still consists of bare tailings (BT) and served as the control in this study.

2.2. Sampling and basic chemical properties of mine tailings samples

Three quadrats (each measuring 3 m by 3 m) were established as triplicate sampling sites for each type of plant. The tailings in the study fields was discarded in approximately 2000, and the *C. zizanoides* plant was artificial planted in 2001, and the *I. cylindrica* and *R. chinensis* colonized the site around the same time. The vegetation directly colonizing the mine tailings received no other management. A portable soil moisture and temperature meter (T200) was used to measure the tailings moisture and temperature. An illuminometer (Tes 1330A) was used to measure the incident photosynthetically active radiation, which was measured 10 cm above the soil, and 10 repeats were calculated as one value in each sample. All measurements were performed in May 2013. In each quadrat, three soil profiles were located randomly, and soil samples were collected from the depth intervals of 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, 40–50 cm and 50–60 cm. Three subsamples from the same depth intervals in the three soil profiles were thoroughly homogenized to form a composite sample. The samples were collected in plastic bags, placed in a cooler with ice and immediately transported to the laboratory. Each sample was divided into three parts in the laboratory. One part was air dried for the analysis of the chemical properties (basic chemical properties, iron oxides and sulfur content), a second was stored at −20 °C for analysis of microbial biomass sulfur and oxygen consumption, and a third part was stored at −80 °C for molecular analysis. The underground biomass of the plants at various soil depths was measured by core methods (Schuurman and Goedewaagen, 1964). Soil cores were obtained at 10 cm intervals to a depth of 60 cm using a heavy soil auger. Soil cores were washed and oven dried weights of roots were recorded after drying at 65 °C for 3 days (Heeraman and Juma, 1993).

The pH value was assessed at a water-to-tailings ratio of 5 using a Mettler Toledo FE20 pH meter. The total organic matter was determined based on the mass loss of ignition (LOI) in a muffle furnace at 550 ± 5 °C for 6 h considering the sulfides in mine wastelands.

2.3. Determination of iron oxides

Free iron oxides (Fe_d) and amorphous iron oxyhydroxide (Fe_0) were measured at 520 nm using a Model 722 spectrophotometer (Jinghua Instruments, Shanghai, China) after extraction by sodium hydrosulfite-sodium citrate-sodium bicarbonate and oxamide, respectively. The crystalline iron oxyhydroxide ($Fe_d - Fe_0$) content was calculated as the difference between free iron oxides and amorphous iron oxyhydroxide. The activity of iron oxides (Fe_0/Fe_d) was calculated as the ratio of amorphous iron oxyhydroxide to free iron oxides (Hseung, 1985).

$$Crystalline\ iron\ oxyhydroxide = Fe_d - Fe_0$$

$$Activity\ of\ iron\ oxides = Fe_0/_{Fe_d} \times 100\%$$

2.4. Determination of the sulfur component

The total sulfur (TS) in the samples was measured using a vario MACRO cube (Elementar, Hanau, Germany) in accordance with the manufacturer's instructions. The total sulfate ion content was determined via ion chromatography after extraction by sodium hydroxide (Yin and Catalan, 2003). The content of reducing sulfur was calculated as the difference between TS and sulfate sulfur.