ORIGINAL ARTICLE

### Influence of litter decomposition on iron and manganese in the sediments of wetlands for acid mine drainage treatments

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Abstract Plant litter will influence the bioavailability of heavy metals in sediments of wetlands used to treat acid mine drainage. To investigate the effect of plant litter on sediments in wetlands and define the comprehensive and continuous role of plant litter, different mass ratios (0%, 5%, 20%) of litter were added into the sediments to study the influence of litter decomposition on the overlying water and sediments. The changes in pH, EC, Eh, Fe, and Mn of the overlying water and the organic matter in the sediments and the forms of Fe and Mn after 1, 7, 14, 21, and 28 days of litter decomposition were studied. The results indicated that litter decomposition increased the pH, EC, and reduced Eh of the overlying water. Litter decomposition promoted the release of Fe and Mn from the sediments into the overlying water and with the continuous decomposition of litter, the concentration of Fe and Mn in the overlying water declined. Litter decomposition increased the content of the organic matter in the sediment, and the forms of Fe and Mn indicated that litter decomposition could significantly affect the transformation of the forms of Fe and Mn. Reducible Fe was the main form in the sediments. Litter decomposition promoted the transformation of reducible Fe, the main form found in the sediments, into

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exchangeable and oxidizable Fe, but had no effect on residual form. Exchangeable Mn was the main form in the sediments, and litter decomposition accelerated the transformation of reducible Mn, most commonly found in the sediments, into oxidizable Mn and had little influence on the exchangeable and residual forms.

Keywords AMD  $\cdot$  Sediments  $\cdot$  Litter decomposition  $\cdot$  Forms of Fe and Mn

#### **1** Introduction

Acid mine drainage (AMD) is a serious environmental issue. It is produced when sulfide minerals which are initially under anoxic conditions are exposed to oxygen and water during mining activities (Akcil and Koldas 2006). In recent years, frequent pollution incidents involving AMD have occurred, and the environment around mining areas has been deteriorated (Mlayah et al. 2009). Currently, several methods, such as the addition of limestone and sodium hydroxide or other alkaline substances, have been used to treat AMD by increasing its pH and reducing its metal concentrations (Madzivire et al. 2010). The typical adverse impacts by AMD are low pH, high concentrations of metals, such as iron, manganese, and zinc in soils (Brantner and Senko 2014; De et al. 2010) and contamination of water quality. Every year, 1.5 billion tons of AMD, which accounts for about 30% of nonferrous metal industrial wastewater, is discharged directly into the environment in China (Luo and Xie 2006). To combat these effects, creating constructed wetlands can remediate AMD by oxidation, precipitation, plant metal uptake, and adsorption of organic matter (Johnson and Hallberg 2005; Salem et al. 2014). Fe and Mn can form insoluble

compounds through hydrolysis and/or oxidation that occur in wetlands and lead to the formation of a variety of oxides and hydroxides into sediments (Karathanasis and Thompson 1995; Batty et al. 2002; Woulds and Ngwenya 2004). Studies have indicated that other heavy metals such as Cd and Cu could be adsorbed on Fe and Mn oxide (Turner and Olsen 2000; Huang et al. 2014), but when oxidation–reduction potential (Eh) decreases or other conditions change, Fe and Mn oxide can be reduced and dissolved, and other heavy metals adsorbed on Fe and Mn oxide can be released into the overlying water and affect the physicochemical properties of the overlying water and the bioavailability of other heavy metals (Zhang et al. 2014; Javed et al. 2013). Therefore, the stability of Fe and Mn in wetland sediments is very important.

Wetland plants that can tolerate a low pH and high concentrations of metals, such as cattail and bamboo, are used in constructed wetlands to remediate AMD (Collins et al. 2005; Nyquist and Greger 2009; Williams et al. 2000; Vardanyan and Ingole 2006; Subrahmanyam et al. 2017). Because of seasonal changes, a large amount of plant litter are produced, which raise the question: can the decomposition of plants in constructed wetlands have a positive effect on the activity and stability of Fe and Mn in the sediments? Whether products of litter decomposition can complex Fe, Mn in sediments and affect the bioavailability of Fe, Mn in sediments remains to be proved. What effect and function does litter decomposition have in constructed wetlands? To date, the accumulation of Fe and Mn in wetland plants is better understood (Williams et al. 2000; Vardanyan and Ingole 2006; Karathanasis and Johnson 2003), but the effect of litter decomposition on Fe and Mn in the sediments is rarely studied, especially in terms of the forms change in Fe and Mn of sediments. Plant litter can produce different substances during different decay times (Dai et al. 2004). Previous studies have focused on the effect of a single type of organic matter by a particular extraction method from litter decomposition on the bioavailability of heavy metals (Zhou and Thompson 1999; Zhang and Ke 2004), and more studies on the process of litter decomposition in relation to heavy metals in sediments are needed. This study focuses on sediments in constructed wetlands, investigating the characteristics and change rules of Fe and Mn in the overlying water and sediments. The aim of this paper was to evaluate the stability and the possible environmental risks of sediments in constructed wetlands treating AMD, which can serve as an information background for scientific management and utilization of sediments and plants in constructed wetlands.

#### 2 Materials and methods

#### 2.1 Sediments and plant litter

In this study, sediments were sampled in the constructed wetland that has successfully been used to treat AMD from abandoned mines in Chafan Village, Zhuchang Town, Guanshanhu District, Guiyang City (Fig. 1). This system purifies AMD through the coupling of plants and microorganisms. Accompanying the purification of AMD, a large amount of reddish-brown sediments has been formed in the constructed wetland. For this study, sediments were collected from the wetland and were naturally dried inside the containers. Then, the sediments were ground to pass a 100 mesh. The physical and chemical characteristics of the sediments were pH 6.46, EC 2180  $\mu$ s cm<sup>-1</sup>, Eh 208 mV, Fe 92 mg g<sup>-1</sup>, Mn 14 mg g<sup>-1</sup>, and the organic matter 25.2 mg  $g^{-1}$ . The plant litter of the experiment is Equisetum ramosissinum which is a vascular plant growing in the constructed wetland. After gently washing and drying of the plant in a drying oven at 65 °C, plant litter was ground to pass a 40 mesh as the experiment materials. The contents of total nitrogen, total phosphorus, Fe and Mn in the plant litter were 0.83%, 0.07%, 2.6 mg  $g^{-1}$  and 0.02 mg  $g^{-1}$ , respectively.

#### 2.2 Experimental design

Ten grams of the sediments was transferred into experiment cups, in which plant litter was added with the mass ratios of 0%, 5% and 20% and denoted as CK, D1 and D2, respectively. A total of 5 batches assigned different time intervals were set up for the trial, and each treatment was set up with 3 parallels. Before the experiment began, 10 mL of deionizer water was added into each experiment cup to activate microbial activity within the sediment samples. For the formal experiment, 30 mL of deionized water was added into each cup and three cups were used for experimental analysis in each treatment at different time periods. The overlying water was poured out from each cup and measured pH, EC, Eh, Fe and Mn at days 1, 7, 14, 21 and 28. The sediments were dried and screened through a 100 mesh to remove litter that had not decomposed. The dried sediments were taken and analyzed to determine the organic matter and the various forms of Fe and Mn in the sediments.

#### 2.3 Analytical method

The pH was measured using a pH meter (PHSJ-3F type, Shanghai REX), and a conductivity meter (DDS11A type, Shanghai Raytheon) and Eh meter (ORP-422 type,





Shanghai SHKY) were used on the same day. The overlying water was filtered through a 0.45-µm microporous membrane, and 10% HNO<sub>3</sub> was added to make the solution pH < 2 before using AAS (WFX-110, Beijing Rayleigh) for the determination of Fe and Mn. Potassium dichromate volumetric method-external heating method was applied for measuring the organic matter in the sediments (Ji 2005). After freeze-drying, 1 g of the sediments was weighed for speciation analysis of Fe and Mn using a modified BCR continuous extraction method (Rauret et al. 1999), and the corresponding forms of Fe and Mn were exchangeable, reducible, oxidizable and residual.

#### 2.4 Statistical analyses

Repeated ANOVA analysis was applied to specify any significant differences in pH, EC, Eh, Fe and Mn of the overlying water and the organic matter in the sediments. Multiple comparisons were performed using the LSD method to compare the effects of plant litter mass on Fe and Mn in the overlying water and sediments. Pearson's correlation was used to analyse the relationship between Fe, Mn forms and pH, EC, Eh of the overlying water and the organic matter in the sediments.

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#### **3** Results

# **3.1** Influence of litter decomposition on the pH, EC, and Eh of the overlying water

In comparison with that in the CK group, litter decomposition affected the pH of the overlying water. As shown in Fig. 2a, the pH was slightly lower in the treatment groups than in the CK group at 1 day (6.41, 6.27 and 6.24 for CK, D1 and D2, respectively). With the continuous decomposition of litter, the pH increased in all groups and reached the highest levels of 6.67 (CK), 6.88 (D1) and 7.58 (D2) at 21 days, and pH values in the D2 group were significantly higher than the D1 and CK groups. The variation in the pH of the CK group was insignificant from 21 to 28 days but pH decreased in the treatment groups. However, repeated ANOVA analysis showed that with the continuous decomposition of litter, pH of the overlying water in different treatments varied significantly (p < 0.01). Multiple results indicated that there was a very significant difference among CK, D1 and D2 (p < 0.01), and that the variation of pH in the overlying water was closely related to the amount of plant litter.

The effect of litter decomposition on the EC of the overlying water was shown in Fig. 2b. The EC of the overlying water in all groups increased sharply from 1 to 14 days, and the D2 group had a range of increase significantly larger than the D1 and CK groups. As shown in Fig. 2b, the increase in the EC of the D2 group was



Fig. 2 Influence of litter decomposition on  $\mathbf{a}$  pH,  $\mathbf{b}$  EC and  $\mathbf{c}$  Eh of the overlying water over time. Each datum represents the mean of triplicate experiments. All error bars represent the standard deviation of triplicate samples

1098 µs cm<sup>-1</sup> at 1 day and 1347 µs cm<sup>-1</sup> at 14 days and the EC changes in all treatment groups were not obvious from 14 to 21 days. From 21 to 28 days, the EC dropped to 794 µs cm<sup>-1</sup> for the D2 group. Repeated ANOVA analysis indicated that EC was significantly different in different treatments (p < 0.05). Multiple results indicated that there was a very significant difference between CK and D2 (p < 0.01), but there was no difference between CK and D1 (p > 0.05).

The effect of litter decomposition on the Eh of the overlying water was shown in Fig. 2c. Litter decomposition significantly reduced the Eh of the overlying water. The Eh in the CK group showed a gradual decrease from -138 mV (1 day) to -167 mV (28 days) In the D1 and D2 groups, Eh reduced to below -200 mV at 1 day, and with the continuous decomposition of litter, Eh in the D1 and D2 groups gradually decreased. Repeated ANOVA analysis showed that with the continuous decomposition of litter, EC of the overlying water in different treatments showed significant differences (p < 0.01). Multiple results indicated that there was a very significant difference among CK, D1 and D2 (p < 0.01).

### **3.2 Influence of litter decomposition** on the concentration of Fe and Mn in the overlying water

Fe and Mn released from the sediments into the overlying water by forming complexes with plant litters. As shown in Fig. 3, decomposition of wetland plant litter influenced the concentration of Fe in the overlying water. The concentration of Fe in the overlying water was 6 mg  $L^{-1}$  in the



Fig. 3 Influence of litter decomposition on the Fe concentration in the overlying water over time. Each datum represents the mean of triplicate experiments. Error bars represent the standard deviation of triplicate samples

D2 group at 1 day, and with the continuous decomposition of litter, it dropped sharply to 0.8 mg L<sup>-1</sup> at 14 days and 0 mg L<sup>-1</sup> at 21 days. In the D1 group the concentration of Fe in the overlying water was 2.5 mg L<sup>-1</sup> at 1 day, and then gradually decreased to 1.5 mg L<sup>-1</sup> at 7 days, and decreased to 0 mg L<sup>-1</sup> at 14 days. The concentration of Fe remained 0 mg L<sup>-1</sup> in the CK group during the experiment. Repeated ANOVA analysis showed that with the continuous decomposition of litter, the concentration of Fe of the overlying water in different treatments varied significantly (p < 0.01). Multiple results indicated that there were significant differences among CK, D1 and D2 groups (p < 0.01).

The influence of plant litter decomposition on the concentration of Mn in the overlying water was shown in Fig. 4. In the D2 group, litter decomposition influenced the concentration of Mn, and it was maximal in the overlying water in the D2 group at 1 day (1.2 mg L<sup>-1</sup>). With the continuous decomposition of litter, the concentration of Mn presented a decreasing trend and decreased to 0 mg L<sup>-1</sup> at 28 days in the D2 group. The changes in the concentration of Mn in the D1 group were not obvious. Repeated ANOVA analysis showed that with the continuous decomposition of litter, the concentration of Mn was significantly different in the overlying water in different treatments (p < 0.01). Multiple results indicated that there was a very significant difference among CK, D1 and D2 (p < 0.01).



**Fig. 4** Influence of litter decomposition on Mn concentration in the overlying water over time. Each datum point represents the mean of triplicate experiments. All error bars represent the standard deviation of triplicate samples

## **3.3** Influence of litter decomposition on the organic matter of the sediments

Organic matter is an important part of sediments and affects and restricts the physical, chemical, and biological characteristics of sediments (Leenheer and Croue 2003; Wu and Tanoue 2001). Maintaining or increasing the organic matter of sediments can promote the formation of agglomerates and maintain their stability (Pulleman and Marinissen 2004). In this study, adding plant litter into the sediments affected the changes of the organic matter of the sediments. As shown in Fig. 5, the organic matter of the sediments in the CK group had little change, but the organic matter was obviously affected in the treatment groups. With the continuous decomposition of litter, the organic matter in the sediments increased and reached 91 mg  $g^{-1}$  in the D2 group at 28 days and had a significantly larger range of increase than that of the D1 group  $(42 \text{ mg g}^{-1})$ . Repeated ANOVA analysis showed that the organic matter in different treatments was very different (p < 0.01). Multiple results indicated that there was a very significant difference among CK, D1 and D2 groups (p < 0.01).

## 3.4 Influence of litter decomposition on forms of Fe and Mn in the sediments

Decomposition of plant litter not only promoted the release of Fe and Mn but also influenced changes in the forms of Fe and Mn. As shown in Fig. 6, the influence of the decomposition of plant litter on residual Fe was not obvious, but litter decomposition promoted a decrease in reducible Fe, and at the same time, exchangeable and



Fig. 5 Influence of litter decomposition on the organic matter of sediments overt time. Each data point represents the mean of triplicate experiments. All error bars represent the standard deviation of triplicate samples



**Fig. 6** Influence of litter decomposition on changes in the forms of Fe in the sediments. Each data point represent the mean of triplicate experiments (note: histograms from left to right were CK, D1 and D2, respectively. The same in Fig. 7)

oxidable Fe increased correspondingly. As shown in Fig. 6, with the continuous decomposition of litter in the sediments, reducible Fe decreased gradually. The reducible Fe in the D2 group was lower than that in the D1 group. Thus, the decrease in the amount of reducible Fe in the D2 group was larger than that of reducible Fe in the D1 group, which decreased from 44.5% at 1 day to 31% at 28 days. Litter decomposition could make exchangeable Fe increase gradually; similarly, exchangeable Fe in the D2 group was larger than that in the D1 group, and the percentage of exchangeable Fe in the D2 treatment group increased from 6.8% at 1 day to 11.6% at 28 days. Oxidable Fe presented a gradually increasing trend with continuous litter decomposition, and the percentage of oxidable Fe in the D2 group increased from initially 8.1% to 19% at 28 days. Fe increased in its oxidable form in all the treatment groups and was larger than that in the exchangeable form. Decomposition of plant litter promoted the transformation of reducible Fe to exchangeable and oxidable Fe in the sediments.

Exchangeable Mn was the main form of Mn in sediments. As shown in Fig. 7, litter decomposition promoted the conversion of reducible Mn to oxidizable Mn, but had little influence on exchangeable and residual Mn. With the continuous decomposition of litter, the Mn content in the reducible form gradually decreased, and the Mn content in an oxidizable form gradually increased. The percentage of reducible Mn in the D1 group decreased from 14.08% at 1 day to 7.04% at 28 days, and the reducible Mn in the D2 group was reduced from 11.47% (1 day) to 2.75% (28 days). Oxidizable Mn in the D1 group gradually increased from 2.96% at 1 day to 12.46% at 28 days, and



Fig. 7 Influence of litter decomposition on changes in the forms of Mn in the sediments. Each data point represents the mean of triplicate experiments

oxidizable Mn in the D2 group increased to 13.73% at 28 days.

#### 4 Discussion

Natural decomposition of wetland plants affected the pH, EC and Eh of the overlying water. During early decomposition, plant litter decomposed and generated lowmolecular organic acids, which made the pH of the overlying water slightly lower than that of the CK group (Zeng et al. 2008; Yadav et al. 2010). As indicated in Fig. 2a, during early plant decomposition, the pH in the D2 group was lower than those in the D1 and CK groups. With the continuous decomposition of litter, the amount of ammonifier increased gradually in a system with additional litter, and ammonia generated by microbial metabolism increased the pH of the system (Zhao et al. 2011). At the same time, litter decomposition generated abundant dissolved organic matter (DOM), which exchanged anions with hydroxide radicals on the surface of sediments and led to an increase in the pH of the overlying water. Abundant litter decomposition from wetland plants released the excess base, resulting in a gradual increase in the pH of the overlying water (Grossl and Inskeep 1996; Yan et al. 1996). Additionally, with a complete release of the excess base from the litter, the pH declined slightly in the overlying water. EC, which is sensitive to chemical forms of dissolved substances, was an important indicator of dissolved ion activity in the water. Studies have shown that ions that significantly contribute to EC contain H<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and Fe<sup>2+</sup>, and EC is relatively sensitive to the chemical forms of dissolved-state matter in

solution (Mccleskey et al. 2012). The decomposition process of plant litter in the study generated rich DOM, which complexed or chelated heavy metals from sediments. The heavy metals were released into the water via the complex or chelation and affected the EC of the overlying water. Studies have also indicated that litter decomposition not only consumes oxygen but also produces reducing substances (Wu et al. 2007). Both oxygen reduction and the production of reducing matter resulted in a decrease in Eh. During early decomposition, abundant water-soluble matter contained in plants was decomposed, and the decomposition of the matter consumed abundant oxygen (Yan et al. 1996); therefore, the Eh dropped during 1-14 days. Then, in the litter, cellulose, hemicellulose and lignin decomposed at a slower pace and with less oxygen consumption (Tang et al. 2005). Consequently, the decline in Eh was relatively moderate after 14 days.

Sediments in constructed wetlands treating AMD contained a large amount of Fe and Mn in different forms and that was released from sediments into the overlying water under certain conditions. Studies have shown that DOM can directly complex or chelate with heavy metals absorbed by the sediments into overlying water (Zong et al. 2015; Christine et al. 2002; Kaiser and Zech 1998). During early litter decomposition, decomposition was completely hydrophilic small-molecular matter, which allowed the formation of high-concentration DOM within a short period (Alken and Leenheer 1993). High-concentration DOM can complex or chelate more Fe and Mn from sediments into the overlying water; hence, the concentrations of Fe and Mn in overlying water reach high levels during early decomposition. During the experiment, Eh was relatively low in the treatment groups, and sulphate-reducing bacterium (SRB) were likely to increase gradually in the sediments (Naresh et al. 2015). Additionally, with  $SO_4^{2-}$ as the electron acceptor, SRB consumed organic acids and generated H<sub>2</sub>S, which formed metal sulphide with the Fe and Mn released from the sediments (Castillo et al. 2012; Li and Liu 2013). In addition, with the extension of litter decomposition time, cellulose and hemicellulose in the litter initially decomposed to form high-molecular organic matter (Zhou and Thompson 1999; Han and Thompson 1999; Kaiser and Zech 1998). Fe and Mn of the overlying water directly complex with high-molecular organic matter to form insoluble complexes in the sediments; this process was one of the factors affecting the reduction in Fe and Mn levels in the overlying water.

Adding plant litter into the sediments resulted in an increase of organic matter. In the early decomposition, litter decomposition generated abundant DOM into the sediments, which increased the amount of sediment organic matter. With the continuous decomposition of litter,

cellulose, hemicellulose and lignin in the litter were decomposed and the organic matter accumulated in the sediments.

The bioavailability and mobility of Fe and Mn depend on their chemical forms, which in sediments are obviously affected by the environment (Kaiser and Zech 1998; Jiang et al. 2006). Not only did the forms of Fe and Mn in D1 and D2 treatment change, but the forms of Fe and Mn in CK group also changed. This indicated that litter decomposition in this study was not the only cause of changes in the forms of Fe, Mn. Some studies show that soil flooding causes changes in the forms of Fe, Mn, and as the flooding time continues, the activity and bioavailability of Fe, Mn in the soil will decrease (Zhang et al. 2014; Perez et al. 2010). In the original sediments reducible Fe was the main form of Fe, while litter decomposition promoted a decrease in reducible Fe as well as an increase in exchangeable and oxidizable Fe. Oxidized Fe forms reducible Fe by generating a Fe oxidation reaction or by Fe coating on the surface of sediments granules. Reducible Fe was characterized by poor stability under reducing conditions and vulnerability to being reduced and dissolved in the environment (Colombo et al. 2014). In this study, decomposition of plant litter consumed oxygen in the water and reduced Eh below - 100 mV. Under a reducing environment, reducible Fe in sediments was dissolved, and the content was reduced; the reduction volume in the D2 group was larger than that in the D1 group. A Pearson's correlation analysis indicated that the Eh correlated significantly with the forms of Fe (p < 0.01). Adding plant litter into the sediments resulted in an increase of the organic matter, and created a reducing environment in which reducible Fe dissolved and released into the sediments solution. Dissolved Fe and Mn bound with organic matter (such as phenolic hydroxyl group, carbonyl, N<sup>-</sup>, and S<sup>-</sup>), and increased the content of Fe in an organic complex and oxidizable form (Yu and Chen 1990; Zhang et al. 2005; Covelo et al. 2007). Additionally, a Pearson's correlation analysis indicated that the organic matter significantly correlated with the forms of Fe (p < 0.01). In this study, the organic matter and Eh found highly significantly correlated with changes in the forms of Fe in the sediments. It was suggested that the organic matter and Eh were the main reasons for the reduction in reducible Fe and the increase in oxidizable Fe. Studies have found that an addition of humus acid increased the content of organic matter in soil and that the content of oxidizable Fe in soil increased with the proportion of humus acid (Zhang et al. 2014). Reduced and released Fe enters an environmental solution and then is re-absorbed to the surface of sediments (Macdonald et al. 2011), resulting in an increase in exchangeable Fe in sediments. Exchangeable Mn was the main form of Mn in the sediments. Decomposition of litter in wetland plants had little

effect on the exchangeable and residual Mn in the sediments, but it promoted the conversion of reducible Mn to oxidizable Mn in the sediments. The correlation analysis results showed that the changes in Eh and organic matter of the sediments during litter decomposition caused the transformation among the different forms of Mn. The decomposition of litter consumed oxygen; thus, the sediments were in reduction condition, and the reducible Mn in the sediments was released. The released Mn formed a precipitate with S<sup>2-</sup> in the environment, making it oxidizable. With the increase in the Mn content, the total amount of Mn in the sediments was small. Therefore, the reduced and dissolved Mn was completely converted into oxidizable Mn, and the effect on exchangeable Mn was small.

Plant litter increased the content of oxidizable Fe and Mn, which can only be dissolved under strongly oxidizing conditions and cannot easily be released in a neutral or weak oxidative environment (He et al. 2003; Luo et al. 2011). The oxidizable Fe and Mn is a relatively stable form in the sediments (Li et al. 2015). Litter decomposition in the constructed wetland promoted the conversion of reducible Fe and Mn to oxidizable Fe and Mn in the sediments, and made the stability of Fe and Mn stronger. The stability of Fe and Mn in the sediments became stronger, which reduced the risk of secondary release of Fe and Mn in the sediments.

#### **5** Conclusions

Decomposition of wetland plant litter can increase the pH, EC and reduce the Eh of the overlying water. In our study, pH and EC of the overlying water in each treatment group increased to the maximum at 21 days and then slightly decreased in each group.

Litter decomposition had an effect on the concentrations of Fe and Mn in the overlying water. With an increase in the amount of litter, the concentration of Fe and Mn in the overlying water showed a downward trend. The Fe concentration in the treatment group decreased to 0 mg  $L^{-1}$  at 21 days; in the D1 group, Fe decreased to 0 mg  $L^{-1}$  at 14 days; Mn decreased to 0 mg  $L^{-1}$  at 28 days in each treatment.

Adding plant litter into the sediments promoted the increase in the organic matter of the sediments. The organic matter in the original sediments was 25.2 mg g<sup>-1</sup>, and with the continuous decomposition of litter, the organic matter in the sediments reached 42 mg g<sup>-1</sup> in D1 group and 91 mg g<sup>-1</sup> in the D2 group at 28 days.

Litter decomposition promoted the conversion of oxidizable to reducible Fe and Mn in the sediments, where Fe was mainly present in the oxidizable form. Litter decomposition caused the transition of oxidizable to exchangeable and reducible Fe, but had no obvious effect on the residual Fe in the sediments. In the original sediments, Mn mainly existed in exchangeable form. As the litter decay time increased, the content of oxidizable Mn gradually decreased, the reducible Mn increased with time, and the decomposition of plant litter occurred. The effect of Mn on the exchangeable and residual Mn in the precipitate was not obvious.

In constructed wetlands used to treat AMD, not only do we choose plants that are resistant to pH, Fe, Mn or other heavy metals, but the biomass of plants must also be considered. High biomass plants can accumulate more heavy metals during their growing period, and during decomposition plant litter promotes heavy metals of sediments immobilized. In practical application, we should keep the litter in the wetland system in its decay period. However, whether plant litter will affect purification efficacy of AMD and whether the litter will still play a fixed role in a longer period of time must be further investigated.

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