Variations in phosphorus speciation in two sets of simulated riparian zones with and without *Perennial* ryegrass were compared. Each set consisted of four units, each measuring 700 mm × 200 mm × 200 mm, which were enhanced with 0, 2.5, 5, and 7.5% red mud (RM) by weight. The levels of total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP) in the effluent were analyzed, and phosphorus fractionation in the media were also determined after the systems had been operational for 3 months. The results showed that the unit received 2.5% RM had the highest rate of phosphorus removal, including TP, TDP, SRP, particulate phosphorus (PP), and dissolved organic phosphorus (DOP) were present at the average concentrations of 0.17, 0.10, 0.07, 0.08, and 0.03 mg/L in the effluent. Sequential phosphorus fractionation showed that calcium-bound phosphorus (Ca–P) was the major component, indicating that the addition of RM induced aluminum/iron-bound phosphorus (Al/Fe–P), which was intensely bioactive, to form intractable Ca–P, which further inhibited the release of phosphorus from the media. However, the presence of *P. ryegrass* had little effect on the removal of phosphorus. Therefore, RM, when used directly in riparian zones at a suitable concentration, is a novel and low cost additive material that can be used to remove phosphorus from reclaimed water.

**Keywords:** Phosphorus speciation; Reclaimed water; Red mud; Simulated riparian zone

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1 Introduction

Red mud (RM), which is generally classified as a solid waste, is generated from the production of alumina by the caustic digestion of bauxite ores [1]. RM, which has a large specific surface area and a homogeneous particle-size distribution, contains Ca, Fe, and Al oxides and other minor constituents [2, 3]. It is usually directly disposed in deposit areas or dumped into the sea, which can result in not only the waste of this resource but also environmental pollution [1]. Recently, some studies have reported various applications for RM, including the removal of nitrates and phosphates, soil remediation at mines, metal recovery [4–6], etc. However, RM is still regarded as a hazardous environmental pollutant due to its highly alkaline properties and high concentrations of various chemical substances [3]. As a consequence, appropriate pretreatment of RM is necessary before practical use [2].

Riparian zones have been widely used for reducing phosphorus pollution due to their low cost, convenient operation, and easy maintenance [7–9]. Adsorption and precipitation of the media is considered to be one of the most useful removal processes of phosphorus from a column of water in riparian zones [10, 11]. Different forms of phosphorus in wastewater, such as soluble reactive phosphorus (SRP), organic-bound phosphorus (Org-P), and particulate phosphorus (PP), and their dynamics have been reported to affect the efficiency of phosphorus removal [12]. However, there are few reports on the use of riparian zones to remove phosphorus from reclaimed water, which generally has a lower phosphorus load. In addition, there are few studies that have focused on variations in phosphorus speciation.

Therefore, a simulated riparian zone was constructed, which was enhanced with different additions of RM in order to treat reclaimed water. The aims of this study were as follows: (1) to investigate the role of RM on the efficiency of phosphorus species removal; (2) to analyze the phosphorus fractionations present in the media; and (3) to identify the effects of plants on phosphorus removal.

2 Materials and methods

2.1 Simulated riparian zone

Two sets of simulated riparian zones were constructed, including one of which grew *P. ryegrass* (noted as V), while the other set, as the
control (noted as C), did not grow any type of grass. Each set contained four small units of polyvinyl chloride (PVC) measuring 700 mm x 200 mm x 200 mm (Fig. 1). Each unit was filled with a mixture of RM and soil as the medium after homogeneous mixing. Due to its strong alkalinity, the pH of RM ranges from 11 to 12, which declines the efficiency of the removal of phosphorus [3]. Therefore, the addition ratios of RM (% wt) in the media were set at 0, 2.5, 5, and 7.5%, which were recorded as 1–4, correspondingly. Thus, the four units in the set with P. ryegrass were noted as V1–V4, and the units in the control were marked as C1–C4, respectively. Each unit was composed of three parts: the first 30 mm of length was composed of coarse gravel (10–20 mm in diameter); the following 640 mm of length was composed of RM and soil (0–4 mm in diameter); and the final 30 mm of length was composed of coarse gravel (10–20 mm in diameter).

2.2 Artificial reclaimed water

The concentration of total phosphorus (TP) in reclaimed water from sewage plants in China is about 1 mg/L. In order to stabilize the quality of the influent, artificial reclaimed water was used in the present study. Phosphorus was obtained by adding KH2PO4 and KH2PO4 (>98% pure) to running water. Al2O3, (NH4)2CO3, H3BO3, NH4NO3, CaCl2, CuSO4, MgCl2, FeCl3, (NH4)2MoO4, and C6H12O6 (>98% pure) were used to provide carbon, nitrogen, and various microelements. Thus, artificial reclaimed water was synthesized that included (in mg/L) 1.2 P, 70 COD, 8 NH4-N, 9 NO3-N, and 12 TN. The artificial influent was delivered to the riparian zone after P. ryegrass had already vigorously grown. The systems were operational for 3 months from July 30 to October 30. During this time, the simulated systems were fed with the artificial reclaimed water once every 2 days, and the hydraulic retention time (HRT) was maintained at about 2 h.

2.3 Monitoring methods

Effluent samples were analyzed for pH, TP, total dissolved phosphorus (TDP), and SRP. The pH was directly measured using a DELTA320 pH meter. TP, TDP, and SRP were determined according to the method described by SEPAC [13]. Based on the concentrations of TP, TDP, and SRP measured in the effluent, the concentrations of PP and dissolved organic phosphorus (DOP) could be derived using the equations PP = TP – TDP and DOP = TDP – SRP, respectively. The surface features and chemical compositions of the RM and soil were examined by scanning electron microscopy (SEM) and electron dispersive spectrometry (EDS) using an Hitachi S-3000N with an EDAX Genesis XM4. The HClO4–H2SO4 digestion method was used to determine the concentration of TP in each media sample [14]. The phosphorus fractions were extracted from each media sample according to the previous procedures [15–17], and consisted of exchangeable phosphorus (Ex-P), aluminum/iron-bound phosphorus (Al/Fe-P), Org-P, calcium-bound phosphorus (Ca-P), and residual phosphorus (Res-P).

2.4 Data analysis

Variations in the amount of phosphorus speciation in the effluent were analyzed by one-way ANOVA using SPSS 13.0 software. The different addition ratios of RM were used as the principal factor and phosphorus speciation was used as the dependent variable. The means were calculated to avoid pseudo-replication, as each addition ratio was assumed to be independent. The significance level was set at 5%. CANOCO software for Windows 4.5 was used to analyze the role of the plants on the removal of phosphorus from the reclaimed water. Log transformations of the data were used to minimize analytical errors. Detrended correspondence analysis (DCA) was conducted on data with different addition ratios that were obtained from RM systems both with and without P. ryegrass in order to determine the length of the gradient along axis 1. The results of the DCA analysis show that the simulated riparian zones were linear, regardless of the different addition ratios of RM, and all of the values obtained using the lengths of the gradients along axis 1 were <3. Therefore, ordination was performed using principal component analysis (PCA).

3 Results and discussion

3.1 Chemical properties of the unused media

The results of the SEM and EDS analysis of the RM and soil are shown in Fig. 2, which indicate that the surface structure and elemental compositions of these two substances are quite different. In comparison with the surface structure of soil, RM has not only a large proportion of voids that are evenly distributed, but also a fine particle size. In RM and soil, oxygen is the predominant element, accounting for 33.99 and 30.38% of the total elemental contents by weight, respectively. Calcium is the second most predominant element in RM, accounting for 26.62% of its weight, whereas, soil has only 2.53% calcium. Iron is the third most dominant element in RM, accounting for 10.26% of the total elements, whereas, iron accounts for just 5.49% of the soil content. Different concentrations of various chemical elements in RM and soil are apt to induce different effects on the removal of phosphorus when used to treat reclaimed water in riparian zones.

The pH of the media has a great effect on the removal of phosphorus from reclaimed water [18]. The pH differed among the simulated riparian zones due to the addition of different ratios of RM to the media (Fig. 3). The pH values of the simulated systems increased as the addition ratio of RM in the media increased. The lowest pH value was found in V1, with an average pH of 8.91, whereas, the
highest appeared in V4, which had an average pH of 9.55. Therefore, the different addition ratios had an extremely significant effect on the pH (F(df = 3) = 90.97; p < 0.01). In situations where the pH ranges from 8.91 to 9.55, calcium and magnesium ions play a critical role in the removal of phosphorus [19]. In addition, the forms of phosphorus that are present in a solution are closely related to pH. When the pH is >7.2, most phosphorus tends to be present in the forms of HPO$_4^{2-}$ and PO$_4^{3-}$, whereas, pH < 7.2, H$_2$PO$_4$ is the predominant form of phosphorus in solution [20]. Moreover, too high of a pH may have a detrimental effect on the growth of plants and reduce the biological activities of microorganisms, which would indirectly lower the removal efficiency of phosphorus [21].

3.2 Variations in phosphorus speciation in the effluent

The concentration of various phosphorus species versus operation time is shown in Fig. 4, which shows great variability due to the different addition ratios of RM that were used in the media. The mean concentration of TP in the effluent was the lowest in V2, which was maintained at 0.17 mg/L, while the highest was measured in V4, which had an average concentration of 0.70 mg/L. The mean concentrations of TP recorded in V1 and V3 were 0.20 and 0.52 mg/L, respectively. Across the entire operation period, TP showed no or only slight dependence on time in V1 and V2; however, TP steadily declined in V3 and V4, from 0.59 to 0.47 mg/L and from 0.77 to 0.62 mg/L, respectively (Fig. 4a).

Variations in the concentrations of TDP (Fig. 4b) and SRP (Fig. 4c) in the effluent are similar to the variations in TP. However, the percentage of SRP in TDP (SRP/TDP) in the effluent fluctuated considerably (Fig. 4d). SRP is one of the sources of phosphorus that is immediately available for biological uptake, and a high concentration of SRP results in the eutrophication of water [22]. The percentage of SRP/TP in the effluent was the highest in V1, reaching 80% on average, whereas, the lowest was measured in V2 with an average of 70%. The mean percentages for SRP/TP were 76 and 78% in V3 and V4, respectively.

The concentrations of PP in the effluent were very different in each of the simulated riparian zones (Fig. 4e). The PP concentration ranged from 0.06 to 0.07 mg/L in V1, from 0.07 to 0.08 mg/L in V2, from 0.19 to 0.29 mg/L in V3, and from 0.31 to 0.41 mg/L in V4. The average concentration of PP in the effluent from V1 was 0.06 mg/L, and demonstrated little dependence on time during the experimental process. The highest concentration of PP was measured in V4, with an average
of 0.35 mg/L. As time passed, the PP concentration declined, similar to the concentration of TP in V3 and V4. PP provides a potential source of phosphorus for the growth of aquatic plants, and PP leads to less eutrophication in natural waters compared with SRP [22].

In V1 and V2, the DOP concentrations of the effluent kept relatively constant with averages of 0.05 and 0.03 mg/L, respectively (Fig. 4f). However, the DOP content of the effluent from V3 and V4 fluctuated dramatically across the entire experimental period. In V3, the concentration of DOP ranged from 0.06 to 0.08 mg/L. In V4, the content of DOP ranged from 0.07 to 0.11 mg/L. DOP is also considered a readily available source of phosphorus for aquatic organisms. DOP more readily results in the eutrophication of water bodies compared with PP because it can be converted into nutrients through enzymatic hydrolysis, especially when the concentration of SRP is low [23].

Under uniform conditions, such as the simulated system employed here, influent concentration, humidity, temperature, etc., the addition ratio of RM significantly affect the removal efficiency of phosphorus from reclaimed water [F(df = 3) = 91.06; p < 0.01]. These results suggest that the best proportion of RM is around 2.5% by weight (V2) for the removal of phosphorus from reclaimed water, as this proportion resulted in the lowest concentrations of TP, TDP, SRP, SRP/TP, and DOP in the effluent and the removal efficiency showed little dependence on operational time. Metal ion concentrations in the effluent of V2 were as follows (in mg/L): Fe (0.56 ± 0.12), Cu (0.38 ± 0.21), and Al (0.60 ± 0.18). The concentrations of other metal ions were too low to be detected, which satisfies landscape water quality standards for concentrations of metals in reclaimed water (GB/T 18921-2002).

### 3.3 Phosphorus fractionation in the media

The concentration and percentage composition of phosphorus in the media that received different addition ratios of RM are shown in Fig. 5. In general, the TP content of the media ranged from 480 to 500 mg/kg before the systems received reclaimed water, including V4 which had the highest average concentration of 498 mg/kg, whereas, V1 and V2 had the lowest average concentrations at 480 and 484 mg/kg, respectively. This indicates that V1 and V2 had strong phosphorus adsorption abilities based on the lower TP content in these media. After treating the reclaimed water, the average increase in the TP contents of V1, V2, V3, and V4 were 80, 102, 55, and 29 mg/kg, respectively (Fig. 5a). In the present study, the amount of TP removed by the media accounted for 81% of the TP removed in V2. Therefore, phosphorus removal is mainly caused by physical, chemical, and biological interactions in the media, which is consistent with the results of previous studies [24, 25].

Ca–P, which is extracted by HCl, is the form of phosphorus associated with calcium minerals. Ca–P is generally unavailable for biological assimilation [26]. Ca–P was the dominant fraction found in the different simulated riparian zones, both before and after the zones received reclaimed water (Fig. 5). High pH values that are usually associated with high calcium levels in the media induced the phosphorus in the reclaimed water to form Ca–P in large quantities. Before this study was conducted, the highest content of Ca–P was measured in V4, reaching 259 mg/kg on average and accounting for 52% of TP; the lowest content was found in V1 with an average of 231 mg/kg and 48% of TP. After the study, the mean content of Ca–P from V2 was the highest at 342 mg/kg and 58% of TP; the lowest content was measured in V1 with an average concentration of 281 mg/kg and 50% of TP.

NaOH-extracted phosphorus contains inorganic (Al/Fe–P) and organic (Org-P). Al/Fe–P represents the phosphorus associated with iron and aluminum oxides, which is the dominant form of inorganic phosphorus especially when a phosphorus deficit occurs [27, 28]. Org–P represents the organic phosphorus associated with humic and fulvic acids which is considered to be resistant to biological decomposition [29]. Before this study, the mean concentration of Al/Fe–P in V1 was the highest, which was measured at 106 mg/kg,

![Figure 4. Phosphorus speciation in the effluent from simulated riparian zones with P. ryegrass. V1, filled squares; V2, filled circles; V3, filled up-triangles; V4, filled down-triangles.](image-url)
whereas, the lowest concentrations were measured in V3 and V4 with average concentrations of 94 and 92 mg/kg, respectively. However, at the end of the study, the average concentration of Al/Fe–P in V1 increased by 7 mg/kg, whereas, the Al/Fe–P concentration declined by 25, 32, and 40 mg/kg in V2, V3, and V4, respectively (Fig. 5). The mean concentrations of Org-P in V1, V2, V3, and V4 increased from 84 to 110 mg/kg, from 79 to 103 mg/kg, from 76 to 80 mg/kg, and from 71 to 74 mg/kg after the reclaimed water was fed, respectively.

Phosphorus, which is extracted by KCl, represents the labile pool of Ex-P. Ex-P is the most chemically reactive element which would be responsible for controlling the phosphorus concentration of natural waters [30]. Ex-P, which was measured at concentrations of less than 50 mg/kg, was comparatively low in all of the simulated systems and independent of the addition ratios of RM (Fig. 5a). Res-P was not extracted by KCl, NaOH, or HCl, which is considered to be a refractory organic phosphorus fraction and biologically unavailable [31]. The mean concentration of Res-P, which was never measured above the concentration of 40 mg/kg, was the lowest phosphorus fraction. Furthermore, Res-P remained at a stable level, and showed less dependence on the addition ratio of RM.

A significant correlation was found between the TP content in the effluent and the concentration of extractable calcium of the media (p < 0.05). An extremely significant relationship was observed between extractable calcium and Ca–P concentrations in the media (p < 0.01). These significant correlations suggest that phosphorus adsorption and precipitation in the media are associated with the concentrations of the poorly crystalline forms of calcium. Moreover, the Ca–P fraction was positively correlated with the amount of RM added to the media, whereas, Al/Fe–P was negatively correlated. Consequently, the addition of RM to the media contributed to the conversion of Al/Fe–P, which is strongly bioactive, to Ca–P, which is much more stable. This could further reduce the release of phosphorus from the media and lower the amount of eutrophication that occurs in water.

3.4 Phosphorus accumulation in plants

In this study, P. ryegrass thrived in V1 and attained an average height of 25 cm. Although P. ryegrass was able to grow in V2, the high pH affected its growth, resulting in dead leaves on some plants and an average height of 23 cm. The survival rate of P. ryegrass in V3 was around 20%, with an average height of just 12 cm. Most of the P. ryegrass in V4 did not survive.

The effect of P. ryegrass on the concentration of phosphorus speciation is shown in Fig. 6. In 1 and 2 the ordination results show a clear separation between simulated systems that did or did not have plants. In 1, which did not receive an addition of RM, the system without plants were predominantly located in the first and second quadrants, whereas, those systems with plants were predominantly distributed throughout the other two quadrants. In 2, the addition of 2.5% RM resulted in the system without plants being located mainly in the second and third quadrants, whereas, the system with plants was predominantly located in the fourth quadrant. In V1 and V2, the concentrations of phosphorus speciation in the effluent were positively correlated with the non-plant systems, but negatively correlated with the plant systems, indicating that plants play an active role in the removal of phosphorus. However, the ordination results obtained by PCA in 3 with 5% RM and 4 with 7.5% RM do not distinguish between phosphorus content in response to the systems with or without plants, as the phosphorus concentration spread out throughout each quadrant. In addition, no correlation could be determined between the concentrations of various forms of phosphorus in the effluent and the presence of plants in each system.

This study shows that plants do not have a critical effect on the removal of phosphorus from riparian zones, which was supported by some researches [32, 33]. The systems with plants (V) had slightly higher phosphorus removal efficiencies than those without plants (C). TP removal from V1 was 5% higher than that of a similar system without plants (C1), and the TP storage in plants was 1.86 g. Analysis by one-way ANOVA showed that the concentrations of phosphorus speciation in the effluent from C1 were slightly, but not significantly, lower than V1 (p > 0.05). Compared with V2, TP removal was 4% lower in C2 and TP storage in plants was 1.57 g. Similarly, the results of the one-way ANOVA analysis indicate that plants did not have a significant effect on phosphorus speciation removal from reclaimed water (p > 0.05). TP removal in C3 was slightly lower than that in V3, and TP storage in plants was just 0.75 g, and the statistical analysis shows that plants did not play a significant role in the removal of phosphorus species (p > 0.05). However, when the RM content was 7.5%, the phosphorus removal efficiency of the system with plants (i.e., V4) was slightly lower than that of the system without plants (i.e., C4), which might have resulted from the stored nutrients in the plants to be rapidly released into the water column during the decomposition.
of detrital tissue following the death of most of the P. ryegrass plants. The role of plants on phosphorus removal decreased with increasing amounts of RM, as the plants were able to take up the monovalent form of $\text{HPO}_4^{2-}/\text{CO}_4$ from the water column, however, when the pH is >7.2, most phosphorus tends to be present in the forms of $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$, which are difficult forms for plants to utilize [20, 34].

4 Concluding remarks

RM contains a large proportion of voids that are evenly distributed, a fine particle size, and a high calcium content of about 26.62% of its weight. The best proportion of RM was determined to be approximately 2.5% by weight, which showed an outstanding capacity for phosphorus species removal from reclaimed water. When the RM content is 2.5% by weight, this optimal pH range, the presence of $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$, and a suitable concentration of calcium in the media improved the removal of phosphorus through the adsorption of media and the assimilation of P. ryegrass in the simulated riparian zones. Moreover, the reasonable addition of 2.5% RM to the media contributed to the conversion of Al/Fe–P (which has an intense bioactivity) to Ca–P (which is more stable), thereby, decreasing the risk of phosphorus being released from the media.

Clearly, RM can be directly used in riparian zones as a novel and low cost material to enhance the removal of phosphorus from reclaimed water in China.

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