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Influence of EMR–Phosphogypsum–Biochar Mixtures on Sudan Grass: Growth Dynamics and Heavy Metal Immobilization

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Abstract: This study investigates the growth dynamics and heavy metal immobilization in Sudan grass cultivated on substrates composed of electrolytic manganese residue (EMR), phosphogypsum, and chili straw biochar. Pot experiments revealed that a substrate with phosphogypsum constituting 75% of the mix hinders Sudan grass seed germination. Compared with sole EMR utilization, the composite substrates notably enhanced plant growth, evidenced by increases in plant height and fresh weight. The integration of these substrates led to a significant elevation in total chlorophyll content (up to 54.39%) and a reduction in malondialdehyde (MDA) levels (up to 21.66%), indicating improved photosynthetic activity and lower oxidative stress. The addition of biochar reduced the content of Zn, Cd, and Mn in the roots of Sudan grass by up to 25.92%, 20.00%, and 43.17%, respectively; and reduced the content of Pb, Mn, and Cr in the shoot by up to 33.72%, 17.53%, and 26.32%, respectively. Fuzzy membership function analysis identified the optimal substrate composition as 75% EMR and 25% phosphogypsum, with 5% chili straw biochar, based on overall performance metrics. This study adopts the concept of "to treat waste with waste". The approach is to fully consider the fertility characteristics of EMR, phosphogypsum, and biochar, underscoring the potential for utilizing waste-derived materials in cultivating Sudan grass and offering a sustainable approach to plant growth and heavy metal management.

Keywords: electrolytic manganese residue (EMR); phosphogypsum; biochar; Sudan grass; heavy metal immobilization; plant growth

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1. Introduction

Electrolytic manganese residue (EMR), a byproduct of acid hydrolysis, neutralization, pressure filtration, and impurity removal processes from manganese carbonate ore, presents significant environmental challenges. With the continuous decline of ore quality, approximately 10–12 tons of waste residue will now be produced per ton of electrolytic manganese [1]. The annual production of EMR reaches approximately 10 million tons, and the stockpile is over 150 million tons [2]. EMR contains essential nutrients like manganese, nitrogen, potassium, and iron, which are crucial for plant growth. These nutrients gradually become bioavailable through weathering processes, suggesting EMR's potential as a substrate for plant growth [3]. However, the high manganese and heavy metal content (including copper, zinc, lead, cadmium, and chromium) in EMR raises concerns about its direct application in agriculture due to the potential for bioaccumulation and subsequent health risks [4,5]. In order to keep the utilization of EMR out of the food chain, it can be applied to the planting of energy crops, which lays a foundation for vegetation restoration in manganese mining areas and the production of raw materials for biofuels on marginal land.

Phosphogypsum is an industrial waste arising from the production of wet-process phosphoric acid. Typically, making 1 ton of phosphoric acid (P_2O_5) can produce 4.5–5.0 tons of phosphogypsum [6]. At present, the stockpile of phosphogypsum in the world is huge, with more than 280 million tons being added every year [7]. Phosphogypsum contains nutrients such as phosphorus, sulfur, calcium, and silicon required for plant growth. Some experimenters have, therefore, applied phosphogypsum as a soil amendment in agricultural production and achieved some valuable results [8–10]. Due to the low porosity of phosphogypsum, soil consolidation may occur after application. At the same time, phosphogypsum also contains a quantity of elements such as cadmium, chromium, and lead. When coupled with its acidity, these pose a risk of heavy metal pollution in agricultural situations [11]. These limiting conditions need to be regulated before using phosphogypsum as either a soil improvement additive or a plant growth substrate.

Biochar, derived from biomass via thermochemical conversion in an oxygen-limited environment, exhibits alkaline properties and nutrient richness, including nitrogen, phosphorus, potassium, calcium, and magnesium. The pore structure and specific surface area of biochar is large [12]. In addition, the cation exchange potential is strong because it has a large number of oxygen-containing functional groups on the surface. Biochar can improve soil structure, increase soil nutrient content, and passivate heavy metal activity. It has been widely studied in the field of soil improvement as a conditioner and for heavy metal pollution remediation [13–15]. Chili is the vegetable with the largest planting area in Guizhou Province; cultivation covered 0.36 million hm^2 in 2021, ranking it first in China [16]. A large amount of chili straw is produced every year, which can be used to prepare biochar, but the fertilizing efficiency and environmental function of the finished products need to be tested.

Sudan grass (*Sorghum drummondii*) is a sorghum of the *Poaceae* family, native to the Sudanese grasslands in Africa. It has advantages such as wide adaptability, strong tillering, high yield, and good stress resistance. It is an energy plant rich in lignocellulose and can be used for fermentation to produce ethanol and biogas [17]. Research has shown that Sudan grass can grow normally in heavy metal-contaminated soil in mining areas, without showing obvious symptoms of toxicity. It has good adaptability, and its cultivation is conducive to the restoration of the local ecological environment [18]. Currently, Sudan grass is mainly planted on agricultural land in traditional ways. Our research poses the following question: based on their respective properties, can we prepare composite matrices of EMR, phosphogypsum, and biochar for growing Sudan grass in order to fully utilize land resources in mining areas? The test was carried out by planting Sudan grass in mixtures of the three ingredients in different proportions through pot experiments in this study. Through the measurement and analysis of relevant indicators, suitable possibilities for the growth of Sudan grass and the control of heavy metal pollution were investigated. The aim of this study is to provide feasible approaches to EMR and phosphogypsum utilization, as well as a theoretical basis for vegetation restoration in these compounds' storage yards.

2. Materials and Methods

2.1. Test Materials

Sudan grass seeds were purchased from Xintian Flower Market in Guiyang City, Guizhou Province, China, and were disinfected by soaking the seeds in 1% H_2O_2 solution for 10 min before using. EMR was collected from the manganese residue yard in Qingxi Town, Zhenyuan County, Guizhou Province, China, with a typical storage time of approximately 12–15 years. After a long period of weathering, it had developed certain fertility characteristics, and some plants were already growing on it. The collected manganese residue was naturally air dried, and, after removing impurities, it was sieved through a 5 mm nylon sieve for later use. Phosphogypsum was collected from a phosphogypsum yard in Kaiyang County, Guizhou Province, China. After the sample was brought back, it was naturally air dried to remove impurities and passed through a 5 mm nylon sieve for later use. Chili straw biochar was home-made in the laboratory. The method was as follows: the chili straw was naturally dried, crushed by a grinder, loaded into a 100 mL porcelain crucible, sealed, and placed in a muffle furnace. It was then heated at 400 °C for 2 h, removed, cooled, put through a 100-mesh nylon sieve, and bagged. The basic chemical properties of the test materials are shown in Table 1.

Table 1. Basic chemical properties of tested materials.

Items	Electrolytic Manganese Residue	Phosphogypsum	Biochar
pH	7.82	5.36	9.38
Organic matter/(g·kg^{-1})	40.63	3.60	402.64
Available N/(mg·kg^{-1})	135.20	8.95	57.28
Available P/(mg·kg^{-1})	7.19	66.42	36.50
Available K/(mg·kg^{-1})	126.85	97.49	103.11
Cu (mg·kg^{-1})	84.92	72.77	12.13
Zn (mg·kg^{-1})	238.75	168.61	32.53
Pb (mg·kg^{-1})	55.37	24.60	19.32
Cd (mg·kg^{-1})	0.28	2.91	0.16
Mn (g·kg^{-1})	38.08	0.63	0.007
Cr (mg·kg^{-1})	407.74	21.88	7.51

2.2. Pot Experiment Design

The experiment was carried out in the greenhouse of Guizhou Education University from 21 May 21 to 29 June 2023. First, the EMR and phosphogypsum were mixed according to different mass ratios (Table 2), and then chili straw biochar was added to a specific treatment at a mass ratio of 5% of the mixture [19], with three repeats for each treatment. The matrix was placed in a flowerpot with a diameter of 21 cm and a height of 15 cm, at a rate of 1.5 kg per pot. The water content of the substrate was brought to approximately 60% of the field capacity by the weighing method. After equilibrating at room temperature for a week, Sudan grass seeds that were large, plump, and of consistent maturity were sown at 15 seeds per pot. The soil water content was maintained at approximately 60% of the maximum field capacity during the plant growing period. The plants were divided into shoot and root parts when harvested. They were then washed with tap water, rinsed with deionized water, wiped dry, and the fresh weight measured. Subsequently, some of the shoot samples were immediately used for the determination of plant physiological indexes. The other parts, together with the roots, were dried at 105 °C for 30 min, followed by drying to a constant weight at 70 °C, and then crushed for later use in the determination of heavy metal content.

Table 2. The different mass ratios that made up the composite substrates.

Treatment	Material Composition/%		
	EMR	Phosphogypsum	Biochar
T1	100	–	–
T2	100	–	+
T3	75	25	–
T4	75	25	+
T5	50	50	+
T6	50	50	–
T7	25	75	+
T8	25	75	–
T9	–	100	+
T10	–	100	–

"–" means none; "+" indicates that biochar was added.

2.3. Determination Definitions and Methods

The emergence rate = number of seeds emerging/number of seeds tested ×100%. The height of Sudan grass was measured with a tape measure. The fresh weight of Sudan grass was measured with an analytical balance. Chlorophyll was extracted with 95% ethanol. The absorbance was measured and the contents of chlorophyll a, chlorophyll b, and total chlorophyll were calculated at 649 nm and 665 nm, respectively. The content of malondialdehyde (MDA) was determined by the thiobarbituric acid colorimetric method [20].

Determination of heavy metal content in the Sudan grass used the HNO_3-H_2O_2 (volume ratio 5:2) system: microwave digestion was carried out at 120 °C (20 min), 160 °C (20 min), and 190 °C (40 min). After acid extraction, transfer, constant volume, filtration, and other procedures, the concentrations of Cu, Zn, Pb, Cd, Mn, and Cr were determined by inductively coupled plasma mass spectrometry (ICP-MS Thermo Scientific (Waltham, MA, USA)), and the content of heavy metals in the sample was calculated [21]. In this procedure, quality control was carried out with plant reference materials (GBW07603 [22]), parallel samples, and blank controls. All reagents used were of very high purity.

2.4. Comprehensive Evaluation

The indexes of different treatments of Sudan grass were comprehensively evaluated by fuzzy membership functions [23]. The calculation formula are as follows:

$$V(Xi) = (Xi - Xmin)/(Xmax - Xmin) \quad (1)$$

$$V(Xi)r = 1 - (Xi - Xmin)/(Xmax - Xmin) \quad (2)$$

In the formulas, $V(Xi)$ represents the membership function values of different indicators; $V(Xi)r$ is the inverse membership function value for different indicators; Xi is the measured value of the ith indicator; $Xmax$ is the maximum value of the measured indicator; $Xmin$ is the minimum value of the measured indicator. A comprehensive evaluation was conducted on the plant height, fresh weight, chlorophyll content, and MDA content of Sudan grass. Except for the MDA content, which was calculated using $V(Xi)r$, the other indicators were calculated using $V(Xi)$. A comprehensive evaluation was also conducted on the inhibition of heavy metal uptake using the Cu, Zn, Pb, Cd, Mn, and Cr contents in the roots and shoots of Sudan grass, and $V(Xi)r$ was calculated backward. Finally, the average value of the membership function of all indexes in the same treatment was obtained, and the average value represented the degree of membership.

2.5. Statistical Analysis

The experimental data was processed using Excel 2019 and expressed as mean ± standard deviation. SPSS 26.0 was used for significance testing (LSD method, $p < 0.05$), and Origin 2018 was used for plotting.

3. Results

3.1. Effect of Compound Substrate on Germination of Sudan Grass

T4 treatment had the highest emergence rate of Sudan grass, reaching 95.56%, significantly higher than the T8–T10 treatments ($p < 0.05$, Figure 1). The lowest was the T8 treatment, which was only 64.44%, significantly lower than the other treatment groups except for T10. In addition, the emergence rate of Sudan grass under treatments T1–T7 was similar, and the difference between them was not significant ($p > 0.05$).

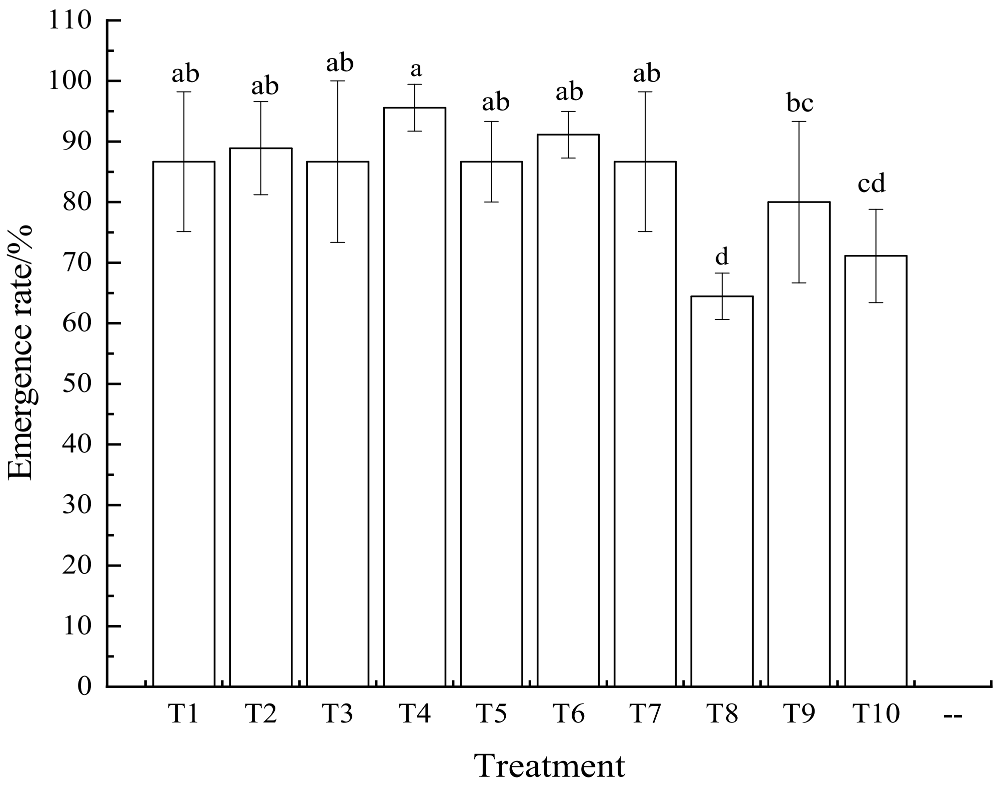

Figure 1. Emergence rate of Sudan grass under different treatments. Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

3.2. Effect of Compound Substrate on Seedling Growth of Sudan Grass

When using phosphogypsum alone as the growth substrate (T10 treatment), Sudan grass began to wilt on the 22nd day after sowing, and, by the harvest time, all seedlings had already died. Based on the appearance (Figure 2), T4 and T6 treatments grew best, with relatively strong stems, broad leaves, and green coloration, while the other treatments looked shorter and had yellowed leaf tips (e.g., T8 and T9) to different degrees. The data in Table 3 show that the plant height of Sudan grass under the T9 treatment was 16.80 cm, which was significantly lower than that of other treatments (the range was 19.20–22.60 cm). It can also be seen from Table 3 that the fresh root weight of Sudan grass under T8 was the lowest (0.18 g·pot^{-1}), which was significantly different from other treatments (p < 0.05). The order of shoot fresh weight under different conditions was T4 > T6 > T2 > T3 > T5 > T7 > T1 > T8 > T9 (Table 3). Among these, the T4 treatment group was significantly higher than other treatments, except T6 and T2. Compared with using EMR as the growth substrate (T1), the total fresh weight of Sudan grass significantly increased by 28.70% to 41.16% when EMR, phosphogypsum, and biochar were mixed according to the proportions in the T2, T3, T4, and T6 treatments (p < 0.05). However, the difference between the four treatments did not reach a significant level (Table 3).

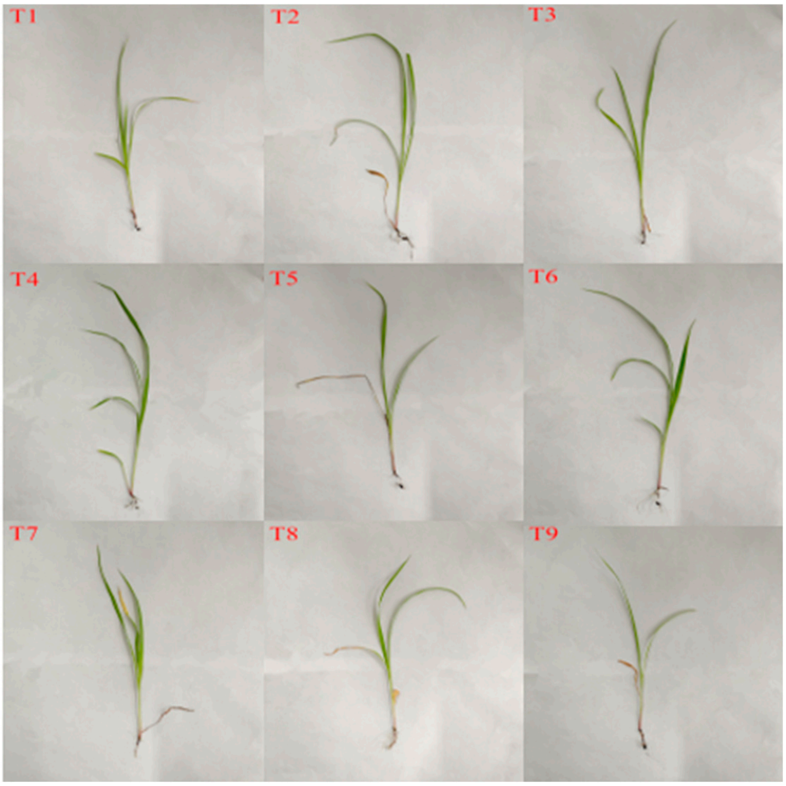

Figure 2. Photos of Sudan grass under different treatments.

Table 3. Plant height and fresh weight of Sudan grass under different treatments.

Treatment	Plant Height/ (cm)	Root Fresh Weight/ (g·pot^{-1})	Shoot Fresh Weight/ (g·pot^{-1})	Total Fresh Weight/(g·pot^{-1})
T1	19.20 ± 2.14 bc	0.28 ± 0.05 bc	0.87 ± 0.07 ef	1.15 ± 0.11 d
T2	19.80 ± 0.97 ab	0.35 ± 0.01 a	1.18 ± 0.10 abc	1.53 ± 0.10 a
T3	20.60 ± 1.19 ab	0.34 ± 0.01 a	1.14 ± 0.05 bc	1.48 ± 0.06 ab
T4	21.70 ± 0.83 ab	0.34 ± 0.01 a	1.28 ± 0.07 a	1.62 ± 0.09 a
T5	19.80 ± 2.58 ab	0.30 ± 0.04 ab	1.06 ± 0.15 cd	1.36 ± 0.17 bc
T6	22.60 ± 2.98 a	0.32 ± 0.01 ab	1.21 ± 0.05 ab	1.53 ± 0.05 a
T7	20.30 ± 1.01 ab	0.28 ± 0.01 bc	0.94 ± 0.09 de	1.22 ± 0.10 cd
T8	19.90 ± 1.16 ab	0.18 ± 0.02 d	0.76 ± 0.04 f	0.94 ± 0.04 e
T9	16.80 ± 0.87 c	0.24 ± 0.05 c	0.61 ± 0.03 g	0.85 ± 0.08 e

Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

3.3. Effects of Compound Substrate on Physiological Indicators of Sudan Grass

The chlorophyll a, chlorophyll b, and total chlorophyll contents of Sudan grass leaves showed different characteristics when grown on different growth substrates (Table 4). The chlorophyll a content ranged from 0.35 to 0.62 mg·g^{-1}, with the T4 to T7 treatment being the highest, followed by the other treatment groups. The T1 and T9 treatments were the lowest. The chlorophyll b content was the lowest in the T9 treatment, only 0.15 mg·g^{-1}, which was significantly different from the other treatments ($p < 0.05$); the T1, T2, and T8 treatments were in the middle, with contents of 0.19–0.20 mg·g^{-1}; the T3 to T7 treatments had the highest content, ranging from 0.25 to 0.27 mg·g^{-1}, and a significant difference compared with the other treatments. In this study, the total chlorophyll content of Sudan grass ranged from 0.50 to 0.88 mg·g^{-1}. Under T3 to T7, the proportion of total chlorophyll significantly increased by 24.56% to 54.59% ($p < 0.05$) compared with using EMR as the growth substrate alone (T1). Among them, the T3 treatment was also significantly lower than T4 to T7, and there was no significant difference with T1 under T2, T8, and T9 conditions.

Table 4. Chlorophyll content of Sudan grass under different treatments.

Treatment	Chlorophyll a/ $(mg \cdot g^{-1})$	Chlorophyll b/ $(mg \cdot g^{-1})$	Total Chlorophyll/ $(mg \cdot g^{-1})$
T1	0.37 ± 0.05 c	0.20 ± 0.02 b	0.57 ± 0.06 cd
T2	0.45 ± 0.04 b	0.20 ± 0.02 b	0.65 ± 0.05 bc
T3	0.44 ± 0.03 b	0.27 ± 0.04 a	0.71 ± 0.03 b
T4	0.58 ± 0.03 a	0.25 ± 0.02 a	0.83 ± 0.05 a
T5	0.57 ± 0.03 a	0.25 ± 0.02 a	0.82 ± 0.05 a
T6	0.59 ± 0.04 a	0.25 ± 0.01 a	0.84 ± 0.03 a
T7	0.62 ± 0.05 a	0.26 ± 0.01 a	0.88 ± 0.05 a
T8	0.39 ± 0.07 bc	0.19 ± 0.02 b	0.57 ± 0.08 cd
T9	0.35 ± 0.02 c	0.15 ± 0.01 c	0.50 ± 0.02 d

Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

Figure 3 shows that the MDA content of Sudan grass showed a significant decrease trend when compared with T1 except for the T2, T5, and T9 treatments ($p < 0.05$), the last of which was close to it. The T3 and T4 treatments had the largest decrease, reaching 21.66% and 21.03%, respectively. However, there was no significant difference between these two treatments and the T6–T8 treatments ($p > 0.05$).

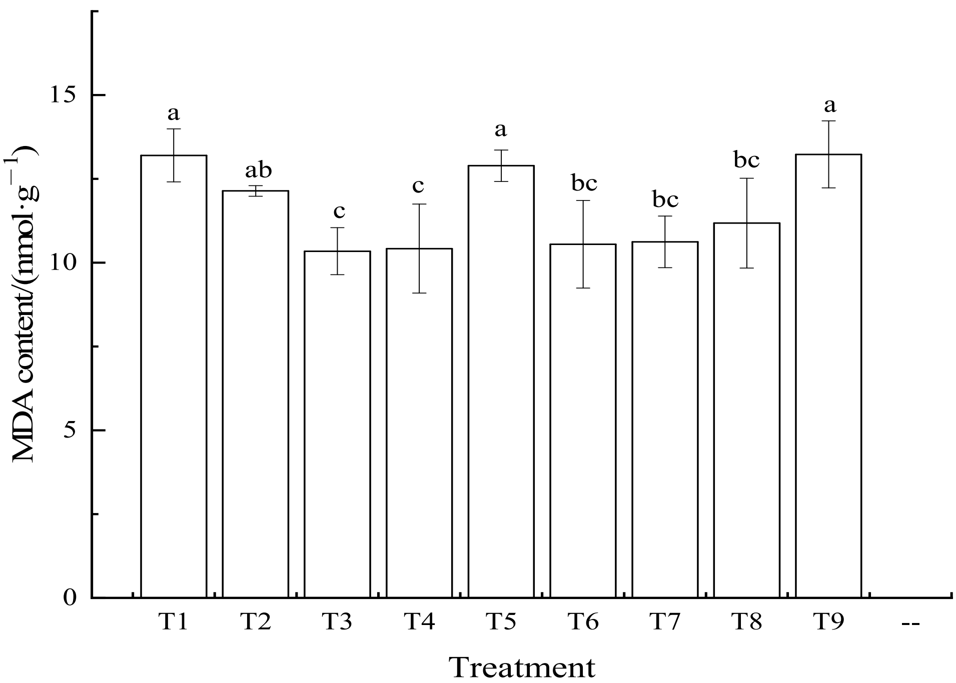

Figure 3. MDA content of Sudan grass under different treatments. Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

3.4. Effects of Compound Substrate on the Absorption of Heavy Metals by Sudan Grass

The heavy metal content of the Sudan grass roots was determined and the results are shown in Table 5. The Cu content under T1 was significantly higher than the other treatments, while the T3 and T9 treatments were significantly lower than the others ($p < 0.05$). The Zn content in the Sudan grass roots ranged from 54.87 to 78.78 $mg \cdot kg^{-1}$, with the T8 treatment being the highest and T9 being the lowest. The difference between the two reached a significant level. For Pb, the root content under T2 (4.23 $mg \cdot kg^{-1}$) was significantly higher than other treatments, while T7 and T9 was the lowest, being only 1.27 and

1.22 mg·kg^{-1}, respectively. The root Cd was the highest (0.35 mg·kg$^{-1)}$) when using EMR as the growth substrate alone (T1 treatment). On the composite substrates, it decreased by 17.14% (T5, T6 treatment) to 45.71% (T9 treatment). The highest Mn content in the roots of Sudan grass was 1625.70 mg·kg^{-1}, but, overall, it decreased between the T1 to T9 treatments, dropping to 395.71 mg·kg-$^{-1}$ at its lowest. The distribution order of Cr content in the roots of Sudan grass was T1 > T2 > T4 > T3 > T8 > T5 > T6 > T9 > T7. Among these, the T1 treatment was 18.12 mg·kg^{-1}, which was significantly higher than other treatments ($p < 0.05$), but the difference between T3 and T5–T9 was not significant. The study also found that except for Cu (T1 and T2 treatments), Mn (T1–T8 treatments), Cr (T1–T6, and T8 treatments), the heavy metal content in the roots of Sudan grass did not exceed the upper limit of normal plant levels (for Cu, Zn, Pb, Cd, Mn, and Cr, these are 45.8, 160, 41.7, 0.8, 400, and 8.4 mg·kg^{-1}, respectively) [24]. Under the same ratio of EMR and phosphogypsum, the addition of biochar reduced the Zn content in the roots of Sudan grass by 6.50% to 25.92% (excluding the T3–T6 treatments). It also reduced the Cd content by 12.00–20.00% (excluding the T3–T6 treatments), and the Mn content by 10.90% to 43.17% (excluding the T7 and T8 treatments).

Table 5. Heavy metal content in root of Sudan grass under different treatments.

Treatment	Cu (mg·kg^{-1})	Zn (mg·kg^{-1})	Pb (mg·kg^{-1})	Cd (mg·kg^{-1})	Mn (mg·kg^{-1})	Cr (mg·kg^{-1})
T1	72.14 ± 3.70 a	69.36 ± 2.99 b	3.47 ± 0.11 b	0.35 ± 0.02 a	1625.70 ± 80.57 a	18.12 ± 1.39 a
T2	53.66 ± 4.88 b	64.85 ± 4.49 bc	4.23 ± 0.30 a	0.28 ± 0.01 bc	1435.57 ± 108.24 b	10.13 ± 0.18 b
T3	32.68 ± 2.26 d	62.64 ± 2.61 cd	1.68 ± 0.06 f	0.22 ± 0.02 de	1266.24 ± 55.27 c	8.99 ± 1.38 bcd
T4	50.12 ± 2.07 b	64.68 ± 1.49 bc	2.04 ± 0.22 de	0.23 ± 0.01 d	719.55 ± 44.87 d	9.77 ± 0.19 bc
T5	42.47 ± 3.06 c	76.75 ± 4.05 a	1.83 ± 0.21 ef	0.29 ± 0.02 b	540.12 ± 40.35 ef	8.74 ± 0.52 cd
T6	42.51 ± 3.52 c	67.43 ± 1.95 bc	2.37 ± 0.12 c	0.29 ± 0.02 b	606.19 ± 29.16 e	8.52 ± 0.41 cd
T7	38.92 ± 1.86 c	58.36 ± 1.52 de	1.27 ± 0.11 g	0.22 ± 0.04 de	467.77 ± 47.16 fg	8.04 ± 0.23 d
T8	44.08 ± 4.37 c	78.78 ± 5.24 a	2.16 ± 0.12 cd	0.25 ± 0.02 cd	454.05 ± 20.85 fg	8.95 ± 0.63 bcd
T9	28.46 ± 1.68 d	54.87 ± 3.32 e	1.22 ± 0.17 g	0.19 ± 0.01 e	395.71 ± 26.25 g	8.33 ± 0.73 d

Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

The heavy metal content of Sudan grass shoots is shown in Table 6. For Cu, except for the significantly low value of the T8 treatment (15.46 mg·kg^{-1}), the contents showed little variation, ranging from 22.42 to 29.10 mg·kg^{-1}. The Zn content under T8 reached 67.47 mg·kg^{-1}, significantly higher than other treatments (23.20–33.71 mg·kg^{-1}). The Pb content of the Sudan grass shoots under T9 (0.98 mg·kg^{-1}) was significantly higher than other treatments ($p < 0.05$), while the T2 and T4 treatments were only 0.57 and 0.60 mg·kg^{-1}, respectively, and were significantly lower than those of the other seven treatments. The highest Cd content was in T6 (0.21 mg·kg^{-1}), which was significantly different from other treatments (0.13–0.18 mg·kg^{-1}). When using EMR as the growth substrate alone (T1 treatment), the Zn content of the Sudan grass shoots was the highest at 309.83 mg·kg^{-1}, then decreased by 17.53% to 56.89% in the composite substrate, the lowest being 173.56 mg·kg^{-1} in the T5 treatment. The distribution order of Cr content in the shoots of Sudan grass was T9 > T8 > T1 > T3 > T7 > T4 > T6 > T2 > T5, which was high at both ends and low in the middle. Among these, the T9 treatment reached 30.24 mg·kg^{-1}, which was significantly higher than that of the other treatments ($p < 0.05$). The Cr content of Sudan grass shoots in all treatment groups exceeded the upper limit of normal plant contents. Under the same ratio of EMR and phosphogypsum, the addition of biochar reduced the Pb content in the shoots of Sudan grass by 13.04% to 33.72% (excluding the T5-T8 treatments), the Mn content by 6.06% to 17.53%, and the Cr content by 16.86% to 26.32%.

Table 6. Heavy metal content in shoot of Sudan grass under different treatments.

Treatment	Cu (mg·kg^{-1})	Zn (mg·kg^{-1})	Pb (mg·kg^{-1})	Cd (mg·kg^{-1})	Mn (mg·kg^{-1})	Cr (mg·kg^{-1})
T1	28.70 ± 1.07 a	23.20 ± 1.24 e	0.86 ± 0.04 b	0.17 ± 0.01 b	309.83 ± 11.01 a	18.73 ± 0.77 b
T2	27.49 ± 2.26 ab	28.22 ± 0.93 cd	0.57 ± 0.04 d	0.18 ± 0.02 b	255.53 ± 12.76 b	13.80 ± 0.84 d
T3	24.69 ± 1.02 bc	29.97 ± 2.14 bc	0.69 ± 0.03 c	0.15 ± 0.02 bc	237.14 ± 19.21 bc	17.26 ± 2.66 bc
T4	25.05 ± 2.21 bc	25.18 ± 2.64 de	0.60 ± 0.02 d	0.17 ± 0.01 b	213.38 ± 9.49 cd	14.35 ± 0.77 d
T5	29.10 ± 2.13 a	30.07 ± 1.49 bc	0.86 ± 0.04 b	0.17 ± 0.02 b	173.56 ± 20.74 f	10.61 ± 0.51 e
T6	26.29 ± 2.08 ab	28.53 ± 1.83 cd	0.83 ± 0.06 b	0.21 ± 0.03 a	184.76 ± 23.04 ef	13.94 ± 1.08 d
T7	26.98 ± 2.55 ab	33.71 ± 2.32 b	0.85 ± 0.03 b	0.16 ± 0.02 bc	194.09 ± 16.20 def	15.39 ± 1.66 cd
T8	15.46 ± 0.56 d	67.47 ± 4.71 a	0.82 ± 0.05 b	0.17 ± 0.01 b	207.69 ± 16.92 de	18.87 ± 0.85 b
T9	22.42 ± 1.32 c	28.10 ± 1.16 cd	0.98 ± 0.09 a	0.13 ± 0.02 c	202.90 ± 10.01 de	30.24 ± 2.19 a

Different lowercase letters indicate significant differences between the different treatments at the 0.05 level.

3.5. Comprehensive Evaluation of the Growth and Heavy Metal Absorption of Sudan Grass

A comprehensive evaluation was conducted on the growth status of Sudan grass, including seedling emergence rate, plant height, fresh weight, chlorophyll, and malondialdehyde content. Fuzzy membership functions were used to calculate the average score (Table 7). Overall, the mean membership function of the growth of Sudan grass under the T4 treatment was the highest, reaching 0.930, while it was the lowest under the T9 treatment, with a mean membership function of only 0.098. The specific order was T4 > T6 > T3 > T7 > T5 > T2 > T1 > T8 > T9.

Table 7. Value of membership function for Sudan grass growth.

Treatment	Membership Function Value										Rank
	Emergence Rate	Plant Height	Root Fresh Weight	Soot Fresh Weight	Total Fresh Weight	Chlorophyll a	Chlorophyll b	Total Chlorophyll	MDA	Mean	
T1	0.714	0.411	0.580	0.388	0.381	0.052	0.451	0.178	0.011	0.352	7
T2	0.786	0.505	1.000	0.856	0.879	0.359	0.386	0.375	0.379	0.614	6
T3	0.714	0.649	0.960	0.791	0.814	0.341	1.000	0.553	1.000	0.758	3
T4	1.000	0.834	0.980	1.000	1.000	0.852	0.861	0.872	0.971	0.930	1
T5	0.714	0.517	0.740	0.672	0.662	0.805	0.828	0.829	0.117	0.654	5
T6	0.857	1.000	0.860	0.891	0.879	0.897	0.847	0.900	0.799	0.881	2
T7	0.714	0.603	0.600	0.488	0.472	1.000	0.934	1.000	0.902	0.746	4
T8	0.000	0.527	0.000	0.219	0.108	0.122	0.324	0.188	0.709	0.244	8
T9	0.500	0.000	0.380	0.000	0.000	0.000	0.000	0.000	0.000	0.098	9

The membership function values heavy metals absorbed by the roots of Sudan grass in each treatment, with larger values indicating smaller amounts of heavy metal absorption (Table 8). The results showed that the range of membership function values for each treatment was 0.108–0.995, and the order was T9 > T7 > T3 > T4 > T6 > T8 > T5 > T2 > T1. Among these, the roots of Sudan grass absorbed the most Cu, Cd, Mn, and Cr under the T1 treatment and the least Cu, Zn, Pb, Cd, and Mn under the T9 treatment.

The membership function values of heavy metals absorbed by the shoots of Sudan grass under different treatment conditions are shown in Table 9. It can be seen that the fluctuation range of the membership function value was generally small, ranging from 0.406 to 0.698. The T4 treatment was the highest and T2 treatment was the lowest; the specific order was T4 > T3 > T2 > T5 > T7 > T8 > T6 > T9 > T1. The Sudan grass shoots under the T9 treatment absorbed the most Pb and Cr, while those under the T1, T5, T6, and T8 treatments absorbed the most Mn, Cu, Cd, and Zn, respectively.

Table 8. Value of membership function for heavy metal accumulation in roots of Sudan grass.

Treatment	Membership Function Value							Rank
	Cu	Zn	Pb	Cd	Mn	Cr	Mean	
T1	0.000	0.394	0.253	0.000	0.000	0.000	0.108	9
T2	0.423	0.582	0.000	0.438	0.155	0.793	0.398	8
T3	0.903	0.675	0.847	0.816	0.292	0.906	0.740	3
T4	0.504	0.589	0.726	0.750	0.737	0.828	0.689	4
T5	0.679	0.085	0.795	0.396	0.883	0.931	0.628	7
T6	0.678	0.475	0.617	0.375	0.829	0.953	0.655	5
T7	0.761	0.854	0.982	0.813	0.941	1.000	0.892	2
T8	0.642	0.000	0.688	0.625	0.953	0.910	0.636	6
T9	1.000	1.000	1.000	1.000	1.000	0.972	0.995	1

Table 9. Value of membership function for heavy metal accumulation in shoots of Sudan grass.

Treatment	Membership Function Value							Rank
	Cu	Zn	Pb	Cd	Mn	Cr	Mean	
T1	0.030	1.000	0.276	0.542	0.000	0.586	0.406	9
T2	0.118	0.887	1.000	0.417	0.398	0.837	0.610	3
T3	0.324	0.847	0.699	0.750	0.533	0.661	0.636	2
T4	0.297	0.955	0.919	0.500	0.708	0.809	0.698	1
T5	0.000	0.845	0.285	0.458	1.000	1.000	0.598	4
T6	0.206	0.880	0.366	0.000	0.918	0.831	0.533	7
T7	0.156	0.763	0.317	0.625	0.849	0.757	0.578	5
T8	1.000	0.000	0.382	0.542	0.750	0.579	0.542	6
T9	0.490	0.889	0.000	1.000	0.785	0.000	0.527	8

4. Discussion

In addition to meteorological factors such as light, temperature, water, and wind, as well as process measures such as cultivar selection, planting mode, watering, and fertilizer management, cultivation substrate is a key factor affecting whether plants can settle in new environments. This study observed a low germination rate of Sudan grass in the T8–T10 treatments, indicating that when the mass ratio of phosphogypsum in the composite matrix reached or exceeded 75%, it was not conducive to the germination of the grass seeds. Plant height and fresh weight are comprehensive indicators of plant growth and can directly reflect the quality of the cultivation substrate [25]. Under the T10 treatment, the Sudan grass plants all died during harvest, indicating that phosphogypsum alone is not suitable as the growth substrate. This may likely be due to its poor structural properties affecting water and gas balance [26] and insufficient levels of organic matter and alkali-hydrolyzable nitrogen (Table 1), which are critical for Sudan grass growth. In addition, the acidic nature of phosphogypsum enhances the availability of heavy metals, and the toxic effect on plants is unavoidable [27].

Conversely, the Sudan grass seedlings treated with T9 survived harvest because the addition of biochar improved the internal environment of phosphogypsum through multiple pathways such as nutrient supply, pH regulation, and heavy metal toxicity regulation [28]. Under the T1 treatment, Sudan grass seedlings did not die during harvest, but their plant height, root fresh weight, aboveground fresh weight, and total fresh weight were all lower than those of the T2–T7 treatments. There are two possible reasons for this phenomenon: first, during the long-term field storage, the EMR used in this study was weathered and mechanically mixed with the soil around the yard. Its properties were quite different from those of fresh manganese residue [29]. It had a certain ability to sustain the growth of Sudan grass, a plant that is tolerant to poor conditions. Second, the nutrients of EMR on its own are incomplete (for example, the content of available phosphorus is low), and the content of heavy metals such as Mn is still high, so the support for plant growth is limited.

Mixing the phosphogypsum with EMR produced a synergy which promoted the growth of Sudan grass seedlings to varying degrees. In addition, although the biomass of Sudan grass in this study was quite different from that reported by Basak et al. [30], the approach has shown a certain potential for growth and development without additional soil cover.

Chlorophyll, vital for photosynthesis, reflects plant health through its concentration [31]. The T4–T7 treatments exhibited the highest chlorophyll levels, indicating optimal substrate mixing for chlorophyll synthesis element availability [32]. Malondialdehyde (MDA) is one of the main products of membrane lipid peroxidation, and its content can reflect the degree of damage to the cell membrane system [33]. It was found that the change of MDA content was opposite to that of the plant growth index as a whole. When EMR was used as substrate alone (T1 treatment), the MDA content of the Sudan grass leaves reached 13.20 nmol·g^{-1}, while in the T4 treatment with the highest total fresh weight, the MDA content was only 10.42 nmol·g^{-1} (Figure 3). This indicates that the mixture of manganese residue–phosphogypsum–biochar at the T4 ratio reduces the generation of strong oxidative lipid peroxides and increases the stability of cell membrane structure.

There are many factors that affect the accumulation of heavy metals in plants, including the type and concentration of elements, plant species, and the parts of the plant where accumulation occurs. The roots, directly in contact with the growth substrate, serve as indicators of the difficulty with which elements are assimilated by the plant. Under the T1 treatment, the heavy metal content of the Sudan grass roots was the highest (excluding Zn and Pb), while under the T9 treatment it was the lowest (excluding Cr). This suggests that heavy metal concentration in the substrate is a crucial determinant of metal uptake in Sudan grass roots. When the ratio of EMR and phosphogypsum in the compound substrate is constant, the addition of biochar can generally reduce the Zn, Cd, and Mn in the roots of Sudan grass. However, similar rules are not seen for Cu, Pb, and Cr, which could be related to the type, content, and interaction of heavy metal elements, the interaction between substrates, and the type and amount of biochar [34]. This needs to be analyzed in detail.

The shoot, the economically valuable part of Sudan grass, is influenced by heavy metal content, affecting its yield, quality, and safe application. In this study, under a particular ratio of EMR and phosphogypsum, the addition of biochar can generally reduce the Pb, Mn, and Cr contents of the Sudan grass shoot, which shows a certain potential for useful applications. It was also found that, except for Cr, the content of heavy metals in the shoots of Sudan grass was lower than that in the root, which was similar to the previous studies [35]. Nevertheless, the Mn and Cr levels in Sudan grass in this study exceeded the upper limit of the normal plant content range, which poses a certain risk of toxicity and needs to be taken seriously. The phenomenon can be explained in two ways. On the one hand, it is related to the production process of electrolytic manganese. During the leaching and impurity removal process, all other heavy metals except Mn react with the sulfurizing agent sodium dimethyl dithiocarbamate to form heavy metal sulfides that enter the EMR and are not easily absorbed by plants [36]. In addition, Cr containing waste is discharged during the secondary pressure filtration and electrolysis process. On the other hand, as predicted by Vásconez-Maza et al. [37] using resistivity tomography and statistical methods, Cr was the most concentrated heavy metal element in phosphogypsum.

Evaluating Sudan grass suitability on various substrates through a single index has limitations [38], so the fuzzy membership function method was used to comprehensively analyze the growth and heavy metal absorption. The results showed that the highest score of heavy metal absorption in Sudan grass root was under the T9 treatment, and the objective reason for this result was the low content of heavy metals except Cr in phosphogypsum. When the proportion of phosphogypsum was high, therefore, the score of this item naturally increased. However, due to the phosphogypsum having insufficient physical and chemical properties for the growth of Sudan grass, the T9 treatment was the worst (Table 7). The scores of growth status and shoot heavy metal absorption under the T4 treatment were the highest, but the root heavy metal absorption score ranked fourth. Considering that the purpose of planting Sudan grass is to restore vegetation in mining areas, to use as livestock feed, or to produce biomass energy, its shoot performance is the characteristic worth the most attention. The T4 treatment can, therefore, be used as a suitable substrate formula for planting Sudan grass, but it is necessary to guard against the inhibition of root growth caused by excessive Mn content.

This indoor investigation underlines the potential of waste-derived substrates for sustainable Sudan grass cultivation, suggesting an effective substrate composition. Yet, validating these findings under field conditions and further exploring the substrate's physical, chemical, and microbial dynamics remain essential. Moreover, considering Cu, Zn, and Mn both as nutrients and contaminants calls for a balanced assessment of their impact on Sudan grass, highlighting the necessity for future research to delineate their safe concentration thresholds.

5. Conclusions

The study demonstrated that Sudan grass seeds face germination and survival challenges in phosphogypsum alone but also encounter high heavy metal content and suboptimal growth in pure electrolytic manganese residue (EMR). Composite substrates consisting of EMR, phosphogypsum, and biochar significantly improved the germination, growth and physiological health of Sudan grass, with the best results at a mass ratio of 75% EMR and 25% phosphogypsum, supplemented by 5% chili straw biochar. These substrates also enhanced photosynthesis and mitigated oxidative stress, as indicated by lower malondialdehyde levels, alongside reducing heavy metal absorption in plant tissues.

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