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Synergistic Passivation of Fly Ash and TMT on Heavy Metals in Sewage Sludge

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Abstract: Large amounts of fly ash and sewage sludge are produced annually in China. The treatment and disposal of such byproducts have become urgent problems that need to be solved. In order to achieve the possibility of realizing land applications for sewage sludge, fly ash and trimercapto-s-triazine trisodium salt (TMT) were used as immobilizing agents, and their passivation effects on four kinds of heavy metals (Cu, Ni, Pb, and Zn) were evaluated. The results showed that the resulting sewage sludge met Chinese standard GB/T23486-2009. When the addition was 10–20% fly ash or 0.4–0.6% TMT, the optimum immobilization effect was obtained. The synergistic passivation of 20% fly ash +0.5% TMT was superior to that of either fly ash or TMT alone. The addition of sewage sludge during the ryegrass growth process significantly increased the plant height, the number of tillers, the chlorophyll content, and the biomass of the ryegrass over the brown soil. The adverse effect of the heavy metals on the ryegrass growth could be alleviated by the passivation effect of fly ash and TMT. The immobilization performance of the fly ash was mainly due to the formation of precipitation and the ion exchange, while that of TMT was due to chelate precipitation.

Keywords: heavy metals; sewage sludge; fly ash; trimercapto-s-triazine trisodium salt; immobilization

1. Introduction

With the acceleration of urbanization in China, the overall output of sewage sludge has been obviously increasing with the rise in the volume of wastewater and its treatment. In 2016, the annual sewage sludge production reached 39.5 million tons (containing 80% moisture) [1]. Sludge accumulation not only occupies a large amount of land, causing environmental pollution, but also is a serious burden for urban sewage treatment plants. Therefore, the reduction, the stabilization, the safe disposal, and the resource utilization of sewage sludge have become urgent problems in China [2,3].

Sewage sludge, a byproduct of biological wastewater treatment processes, is rich in organic matter (OM), nitrogen (N), phosphorus (P), and other trace elements. Its land applications include the facilitation of the recycling of nutrients for accelerating plant growth and improving soil characteristics, such as porosity, bulk density, and water retention capacity [4–6]. However, sewage sludge might contain toxic heavy metals, and the long-term use of sewage sludge on the land would inevitably result in the accumulation of toxic levels of heavy metals in the soil, which is considered to be the main obstacle for the practical application of sewage sludge on the land [7].

Many studies have been conducted to immobilize the heavy metals in sewage sludge [8,9]. The presence of such heavy metals could be decreased via reactions with chemical passivating agents through precipitation, chelation, sorption, and ion exchange. The generally used agents include alkaline compounds, aluminosilicates, phosphorus-containing materials, and sulfides [10].

Fly ash, a byproduct produced in coal-fired power plants, is mainly composed of SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, unburned carbon, and sulfate (SO_4^{2-}) [11]. Its irregular accumulation and improper disposal have allowed it to contaminate large areas of land, resulting in the degradation of the soil and increased risk to both human health and the environment. Fine particles of fly ash, small enough to escape emission control devices, are easily suspended in the air and have become a main source of air pollution. In 2016, the fly ash output in China was 5.65 billion tons [12]. The huge quantity of fly ash produced annually poses serious environmental concerns. China's relatively rich coal deposits mean that coal is likely to be the dominant fuel for the generation of power in China for a long time in the future. Thus, developing appropriate measures for the safe disposal of fly ash and discovering practical means of utilizing fly ash are very necessary for sustainable management [13].

In recent years, many scientific studies have been conducted relating to up-cycling technologies for fly ash, which, in turn, have significantly increased the value-added applications of fly ash [14–16]. Fly ash, being mostly alkaline, can transform heavy metals in the soil into a stable state, and it has been widely used to remediate heavy metal-contaminated soil [17,18]. Practical applications of fly ash on the land can improve the physical properties of the soil, including the texture, the bulk density, the and water retention capacity [19,20]. Fly ash contains most of the essential plant nutrients except OM and N [11], while sewage sludge is rich in OM and N. Thus, the mixture of fly ash and sewage sludge would not only provide appreciable amount of nutrients for plant growth, but would also immobilize the heavy metals in sewage sludge. The application of such a mixture on the land could, therefore, benefit the environment and ecology by enhancing the plant yield and solving the disposal problem regarding fly ash and sewage sludge.

In order to improve the stabilization effect on the heavy metals in sewage sludge, trimercapto-s-triazine trisodium salt (TMT) was combined with fly ash. Their synergistic passivation effect on the heavy metals and their impact on plant growth needed to be systematically studied. The objectives of this study were as follows: (1) to investigate the properties of sewage sludge and fly ash to evaluate whether they are appropriate for land application, (2) to evaluate the immobilization effect of fly ash and TMT on the heavy metals in sewage sludge, (3) to compare the effect of immobilized and un-immobilized sewage sludge on ryegrass growth, and (4) to analyze the passivation mechanism of fly ash and TMT on the heavy metals in sewage sludge. The effective immobilization of the heavy metals in sewage sludge could solve the problem of the pollution caused by heavy metals during the process of the land use of sewage sludge. At the same time, this proposal provides a new idea for the resource utilization of fly ash.

2. Materials and Methods

2.1. Collection and Preparation of the Materials

The dewatered sewage sludge (15–20% dry solid content) was collected from the Changqing Wastewater Treatment Plant in Ji'nan, Shandong Province, China. Before the sewage sludge was de-moisturized via centrifuge, a large amount of CaO was added to make the sewage sludge easier to dewater and to reduce the pathogens and the availability of the heavy metals. The dewatered sewage sludge was air dried, homogenized, and crushed by a grinder. The fly ash was obtained from a coal-fired thermal power plant in Ji'nan. Brown soil from the campus of Qilu University of Technology was selected for the plant growth experiment. All the samples of soil, sewage sludge, and fly ash were passed through a 60 mesh sieve for further analysis and the plant cultivation experiment.

The TMT, chosen as an organic sulfur passivating agent, was obtained from Xinjiang Environmental Protection Materials Co., Ltd. in Lianyungang, Jiangsu Province. The TMT was 15% aqueous solution, which could form stable precipitation with 1 valence and 2 valence metal ions, such as Ni^{2+}, Pd^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, and so on.

2.2. Analytical Methods

2.2.1. Determination of the Physico-Chemical Properties

The pH value was determined in a 1:5 (w/v) suspension of the solid sample and distilled water using a pH meter. The OM, electricity conductivity (EC), cation exchange capacity (CEC), and moisture content were analyzed by the standard laboratory procedures. Total nitrogen (TN) was measured by semi-micro Kjeldahl method. Total phosphorus (TP) was determined by Mo-Sb colorimetric method, after the sample was digested by H_2SO_4-$HClO_4$. Total potassium (TK) was determined by an alkaline fusion–flame photometric method [21].

2.2.2. Extraction and Determination Methods for the Heavy Metals

The total concentrations of the heavy metals were determined by digesting a known quantity of the sample using HNO_3-H_2O_2 [22]. The acid digestion suspensions were then filtered through a filter membrane (0.45 μm), and the filtrates were measured to determine the total metal concentrations by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000DV, Perkin Elmer, American).

The chemical fractions of the heavy metals were measured by the four-stage Community Bureau of Reference (BCR) sequential procedure. The BCR procedure was basically a revised method of the five-stage sequential extraction procedure initially put forward by Tessier et al. [23–25]. It has been widely used in the assessment of metal bioavailability in various matrices (e.g., sediment [26,27], soil [28,29], sludge [30,31], ash [32,33] and other industrial residues [34–36]). In this paper, a modified BCR process was used to analyze the speciation of the heavy metals in sewage sludge, brown soil, and fly ash. During the extraction process, the heavy metals in each sample were classified into four fractions—the exchangeable fraction, the reducible fraction, the oxidizable fraction, and the residual fraction—land each fraction showed different bioavailability. The exchangeable fraction, combined with carbonates, was easily migrated into the soil solution and considered to be bioavailable. The reducible fraction and the oxidizable fraction were potentially bioavailable. The residual fraction was thought to be unavailable to plants [37,38].

The extraction steps are shown in Figure 1.

The supernatant obtained by the extraction process was treated by the previous method for the determination of the total concentrations of the heavy metals. For each extraction step, a blank experiment was conducted with an equal amount of the different reagents. All the containers in the experiments were previously soaked overnight with 20% (v/v) HNO_3 and then rinsed with ultrapure water. All the reagents were of analytical grade and contained very low concentrations of trace metals. The ultrapure water was from a Millipore Milli Q system. Normal precautions for trace metal analysis were observed throughout the process.

A check of the results of the modified BCR process was conducted by comparing the sum of the four fractions with their total concentrations. The results indicated that the sum of the four fractions was consistent with the total heavy metal concentration, which showed that the modified BCR sequential extraction procedure used to determine the speciation of the heavy metals in the fly ash, sewage sludge, and brown soil was reliable.
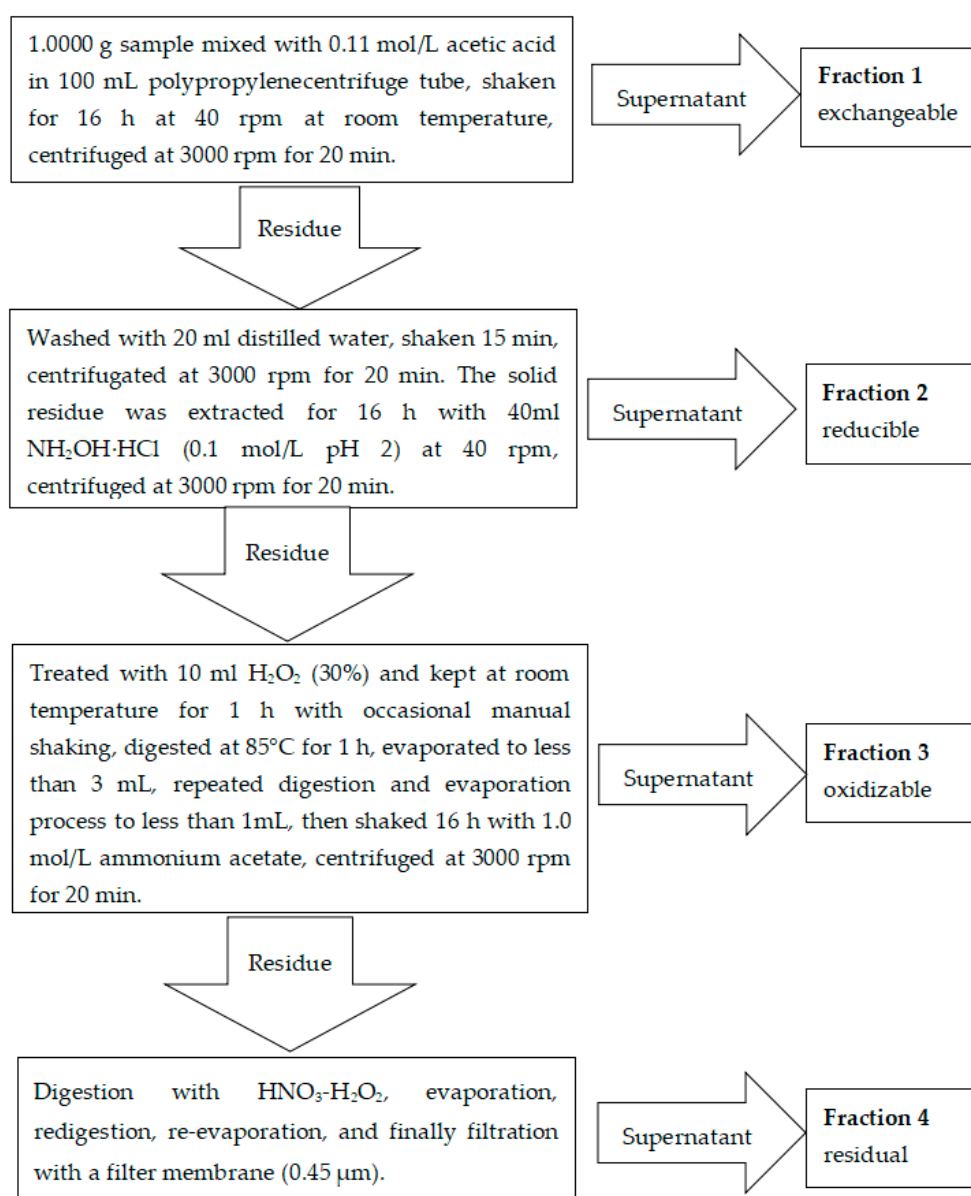
Figure 1. Community Bureau of Reference (BCR) sequential extraction procedure.

2.3. Immobilization Treatment of the Sewage Sludge

Fly ash was mixed with the dewatered sewage sludge at the weight proportions of 0%, 10%, 20%, 30%, and 40%, respectively. After being mixed evenly, the mixtures were maintained at 50% water content for 5 days at room temperature to ensure the complete immobilization of the heavy metals in the sewage sludge. They were then air dried, homogenized, and crushed by a grinder. Then, they were passed through a 60 mesh sieve for further analysis and the plant cultivation experiment. The samples were labeled as F0, F10, F20, F30, and F40, respectively.

The air-dried fly ash–sewage sludge mixtures were mixed thoroughly with the brown soil at the weight proportion of 1:4. In order to achieve the blending homogeneity of the fly ash, sewage sludge, and brown soil, an appropriate amount of distilled water was poured into the mixtures and then air dried at room temperature. The process was conducted three times to ensure that the mixtures were blended thoroughly.

A 15% TMT solution was mixed with the sewage sludge slurry (50% water content) at the weight proportions of 0%, 0.2%, 0.4%, 0.6%, and 0.8%, respectively. Because TMT could react with the heavy

metal ions rapidly, the passivation time was not considered. The mixtures were air dried, homogenized, and crushed by a grinder. Then, they were passed through a 60 mesh sieve for further analysis and the plant cultivation experiment. The samples were labeled as T0, T0.2, T0.4, T0.6, and T0.8, respectively.

The synergistic immobilization of the fly ash and TMT on the heavy metals was investigated by adding 0.5% TMT into sample F20. The sample treated by 20% fly ash and 0.5%TMT was labeled as F20T0.5.

The speciation change of the residual heavy metals (Δresidual fraction) was obtained by subtracting the percentage of residual fraction in the raw sewage sludge from the percentage of the residual fraction in the immobilized sewage sludge. If the value was positive, it meant that the residual state had increased, and the immobilization effect on the heavy metals had improved. The larger the positive value, the better the passivation effect. On the contrary, if the value was negative, it could be concluded that part of the residual fraction was activated by the treatment.

The speciation change of the exchangeable heavy metals (Δexchangeable fraction) was obtained by subtracting the percentage exchangeable fraction in the immobilized sewage sludge from the percentage exchangeable fraction in the raw sewage sludge. If the value was positive, it meant that the exchangeable fraction increased, and the treatment had a certain passivation effect on the heavy metals. If the value was negative, it could be concluded that the heavy metals were activated.

2.4. Ryegrass Planting Experiment

The prepared samples of brown soil and sewage sludge were filled into flowerpots (21 cm × 49 cm × 20 cm). The three treatments, including the control treatment, the un-stabilized sewage sludge treatment (USS), and the stabilized sewage sludge treatment (SSS) are shown in Table 1, and there were three replications for each treatment. No fertilizer was applied before and during the planting experiment. The ryegrass, in good health and the same age, was collected from campus' lawn in the same size, including the area, height, and biomass. The flowerpots were placed in a glasshouse at 25–30 °C and 50–70% relative humidity and ensured 14 h of natural daylight per day. The plants were permitted to grow for 42 days. These flowerpots were watered using distilled water daily to maintain 70% of the field water retention capacity. In each parallel treatment, 10–12 strains were selected randomly to measure their plant height, the number of tillers, and the chlorophyll content. The chlorophyll content was determined by an ethanol extraction method [39,40]. The aboveground part was used to determine the biomass, including the fresh weight and dry weight.

Table 1. The proportions of the various substrates used in the three treatments.

Treatment	Brown Soil	Sewage Sludge	Fly Ash	TMT
Control treatment	100%	0	0	0
USS treatment	80%	20%	0	0
SSS treatment	79.50%	16%	4%	0.50%

Each value represented on an air-dried weight base. TMT: trimercapto-s-triazine trisodium salt; USS: un-stabilized sewage sludge; and SSS: stabilized sewage sludge.

3. Results and Discussion

3.1. Characteristics of the Sewage Sludge, Fly Ash, and Brown Soil

The physico-chemical properties and heavy metal contents of the selected fly ash, sewage sludge, and brown soil are listed in Table 2. The pH value of the sewage sludge was 6.89 ± 0.13, which was close to the pH of the brown soil (6.82 ± 0.04); therefore, the land use of the sewage sludge would have little effect on the pH of the soil. The pH value of the fly ash was as high as 10.88 ± 0.02, which was mainly due to its high content of CaO and MgO [41]. The high pH value was beneficial to transform the active heavy metal fraction into the residual fraction and helped to reduce their bioavailability [17,42]. Thus, fly ash has been commonly used as a kind of passivating agent to stabilize heavy metals.

Table 2. Physical and chemical properties of the sewage sludge, fly ash, and brown soil.

Samples	Sewage Sludge	Brown Soil	Fly Ash
pH	6.89 ± 0.13	6.82 ± 0.04	10.88 ± 0.02
Electricity conductivity (EC) (mS/cm)	1.92 ± 0.064	0.11 ± 0.004	0.57 ± 0.04
Cationexchange capcity (CEC) (mmol/kg)	142.52 ± 3.48	30.00 ± 13.00	79.59 ± 2.06
Organic matter (g/kg)	392 ± 12	17.87 ± 0.46	3.82 ± 0.45
Total nitrogen (TN) (g/kg)	19.37 ± 2.53	0.15 ± 0.05	0.007 ± 0.001
Total phosphorus (TP) (g/kg)	17.14 ± 1.87	0.35 ± 0.04	1.51 ± 0.21
Total potassium (TK) (g/kg)	5.23 ± 1.34	5.24 ± 1.06	7.34 ± 1.26
Cu (mg/kg)	92.50 ± 13.79	13.88 ± 3.42	18.8 ± 1.45
Ni (mg/kg)	50.20 ± 7.92	16.74 ± 1.99	13.83 ± 2.57
Pb (mg/kg)	42.70 ± 5.37	7.28 ± 1.17	15.53 ± 3.11
Zn (mg/kg)	1901.00 ± 36.00	76.99 ± 6.35	57.09 ± 5.24

The EC values of the sewage sludge and fly ash were 1.92 ± 0.064 mS/cm and 0.57 mS ± 0.04/cm, respectively, which were much higher than that of the brown soil (0.11 ± 0.004 mS/cm). Their land application would increase the EC of the soil and was undesirable for plant growth. But, the EC values of the two components were both less than 2 mS/cm, meeting the requirements for the EC level in the Chinese national standard "Disposal of sludge from municipal wastewater treatment plant—Quality of sludge used in gardens or parks" (GB/T23486-2009).

The CEC values of the sewage sludge and fly ash were 142.52 ± 3.48 mmol/kg and 79.59 ± 2.06 mmol/kg, respectively. The higher CEC value meant better buffering capacity and moisture-holding capacity. Thus, their addition would help to improve the soil properties.

The effect of the sewage sludge and fly ash on the chemical properties of the soil depended on their composition. The contents of the OM, TN, and TP in the sewage sludge were 21.9, 129.1, and 49.0 times those in the brown soil, respectively. The TK content in the sewage sludge (5.23 ± 1.34 g/kg) was similar to that of the brown soil. The high nutrient contents could provide essential OM, N, and P for plant growth. Applying the appropriate amount of sludge to the soil can effectively improve the chemical properties of the soil and make full use of the effective nutrients in sewage sludge. Thus, the land application of sewage sludge has been considered to be an effective method for its treatment and disposal [10,43,44]. The contents of the TP and TK in the fly ash were 1.51 ± 0.21 g/kg, and 7.34 ± 1.26 g/kg, respectively. Both of the values were higher than those in the brown soil, while the contents of the OM and TN in the fly ash were in negligible quantities. At the same time, the fly ash was reported to contain not only some macro-nutrients (Ca, Mg, and S), but also some micro-nutrients (Cu, Zn, Mn, and Fe), which were essential to plant growth [20,45,46]. Because of the contrasting and complimentary nutrient contents of fly ash and sewage sludge, their cooperation could provide more benefits in increasing soil fertility and improving the soil properties than either the fly ash or the sewage sludge alone.

High concentrations of heavy metals in the soil might influence the microflora and inhibit the activity of the enzymes in the soil. Thus, the presence of heavy metals in sewage sludge has restricted its land application. In order to reduce the environmental risk, many countries have formulated national standards limiting heavy metals in sewage sludge for land application uses. The contents of Cu, Ni, Pb, and Zn in the sewage sludge were 92.50 mg/kg, 50.20 mg/kg, 42.70 mg/kg, and 1901.00 mg/kg, respectively, which were below the limits of GB/T23486-2009. Thus, the results met the national standards for land application uses. In particular, the addition of fly ash could increase the pH value and form the precipitation in a metal hydroxide form. Therefore, the cooperation of the two components may not only improve the physico-chemical properties of the soil, but also reduce the bioavailability of the heavy metals in sewage sludge.

3.2. Immobilization of the Fly Ash on the Heavy Metals in the Sewage Sludge

The speciation of heavy metals is a more important factor in determining the mobility, bioavailability, and eco-toxicity of a product than the total concentrations of heavy metals. The bioavailability and eco-toxicity of the heavy metals were significantly reduced as their mobile and bioavailable fractions were transformed into the relatively stable fractions [47]. The immobilization effect of the fly ash on the heavy metals in sewage sludge is shown in Figure 2.
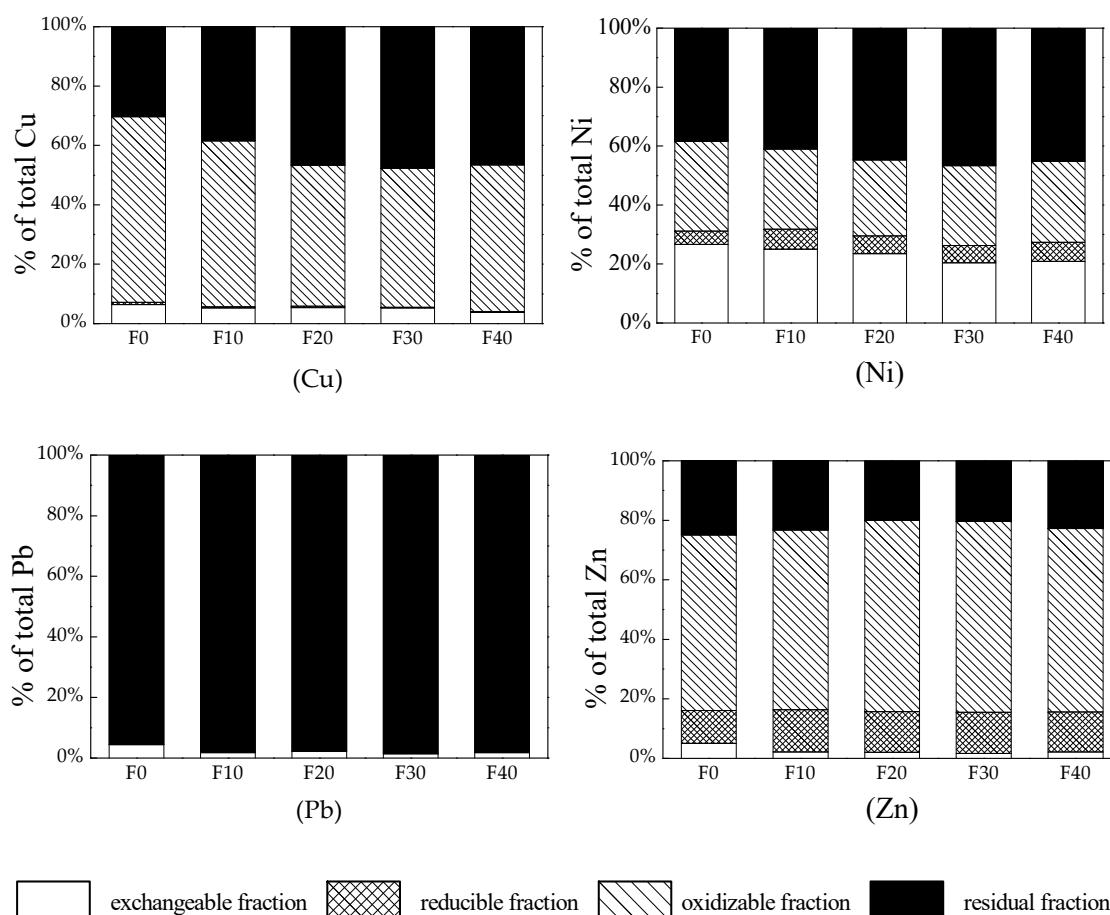
Figure 2. Passivation effect of the fly ash on the heavy metals in the sewage sludge.

Cu was mainly in the residual fraction and the oxidizable fraction in the sewage sludge. The residual Cu increased after the addition of the fly ash. When the added amount of fly ash was 20%, the residual Cu increased from 30.29% to 47.68%, and the oxidizable fraction decreased from 62.58% to 47.50%. The decreased oxidizable Cu was mainly converted into residual Cu. As the fly ash addition further increased, the residual Cu and oxidizable Cu changed little, while the exchangeable fraction continued to decrease. When the addition of the fly ash reached 40%, the proportion of the exchangeable Cu reduced to 3.77% and was principally converted into oxidizable Cu.

Ni was mostly in the exchangeable state, the oxidizable state, and the residual state. The residual Ni increased from 38.34% to 45.67%, and the exchangeable Ni reduced from 26.65% to 23.51% when the addition of the fly ash was 20%. The exchangeable Ni continued to decrease with the increasing fly ash addition. When the added fly ash increased to 40%, the ratio of the exchangeable Ni decreased to 20.87%.

The exchangeable Pb and residual Pb in the sewage sludge were 4.42% and 95.58%, respectively. The reducible Pb and oxidizable Pb were both lower than the detection limit. The exchangeable Pb reduced from 4.44% to 1.77% and the residual Pb increased from 95.58% to 98.23% when the addition

of the fly ash was 10%. Even as the addition of the fly ash continued to increase, the residual Pb increased little. Thus, the suitable addition of fly ash for the Pb immobilization was 10%.

Zn mainly presented in the reducible fraction, the oxidizable fraction, and the residual fraction. The exchangeable Zn reduced with the increase of the addition of the fly ash. The exchangeable Zn reduced from 5.10% to 2.16%, and the reducible Zn increased from 11.04% to 14.25% by adding 10% fly ash. The exchangeable Zn was converted into reducible Zn, which helped to reduce the mobility of Zn. However, proportion of the residual Zn was transformed into oxidizable Zn, which was not conducive to Zn immobilization.

The results indicated that the fly ash showed different passivation effects on the selected heavy metals in the sewage sludge. Good fixation effects on Cu and Pb could be obtained by adding the proper amount of fly ash, while the fixation effects on Ni and Zn were poor. When the addition of the fly ash was 10–20%, the best fixation effect was obtained.

Fly ash is a heterogeneous mixture, composed of amorphous vitreous and crystal minerals, such as quartz and mullite. It mainly consists of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, and so on. Iron oxides can combine with heavy metals to form an iron–manganese bound state, and alkaline materials such as CaO and MgO are beneficial to the formation of the iron–manganese bound fraction and the residual fraction. The addition of fly ash helps to decrease the mobility of the heavy metals in sewage sludge. In this study, the application of the fly ash increased the contents of the residual Cu, the residual Ni, the residual Pb, the reducible Ni, and the reducible Zn, and the exchangeable fractions of the four heavy metals and the oxidizable Cu fraction deceased. Moreover, the fly ash contained little OM, and its addition led to the reduction of oxidizable Cu and oxidizable Ni.

Fly ash generally has strong adsorption properties and a large specific surface area, which helps it to form covalent bonds with heavy metals ions [48]. Bian et al. obtained a modified fly ash with a larger specific surface area and a lot of active groups by using a microwave/alkali method. The passivation performances of the modified fly ash on the exchangeable Cu, the reducible Cu, oxidizable Cu, and the residual Cu were 18.1%, 24.48%, 33.25%, and 249.19% higher than the unmodified fly ash, respectively [49]. In this experiment, the specific surface area of the used fly ash was only 2.09 m^2/g, which was similar to that of sewage sludge. This indicated that the immobilization of the fly ash for the selected four heavy metals was mainly due to the formation of precipitation under high pH conditions and the transforming into the iron–manganese reducible fraction.

3.3. Immobilization of the TMT on the Heavy Metals in the Sewage Sludge

TMT is an organic sulfur compound, produced by the reaction of 2,4,6-trithione-1,3,5-triazine in an alkaline solution. Its special sulfur group can form chelate precipitation by combining with heavy metals. Matlock et al. used TMT to form stable precipitation with Cd^{2+}, Pb^{2+}, and Zn^{2+}, and no decomposition products were detected in the leached solid residues [50]. Thus, TMT has been widely used in the treatment of wastewater containing heavy metals [51,52]. The immobilization effect of the TMT on the heavy metals in the sewage sludge is shown in Figure 3.

The exchangeable Cu and the oxidizable Cu decreased and were transformed into residual Cu by adding the TMT. The residual Cu increased from 30.29% to 38.40% when 0.4% TMT was added. The content of the reducible Cu changed little by increasing the addition of the TMT. When the TMT addition exceeded 0.4%, its immobilization effect on Cu was not be enhanced. Thus, the optimum dosage of the TMT for the Cu immobilization was 0.4%.

The TMT addition decreased the exchangeable Ni and the reducible Ni, while the residual Ni increased little. The exchangeable Ni and the reducible Ni was transformed into oxidizable Ni. The oxidizable Ni increased from 30.55% to 40.46% when 0.4% TMT was added.
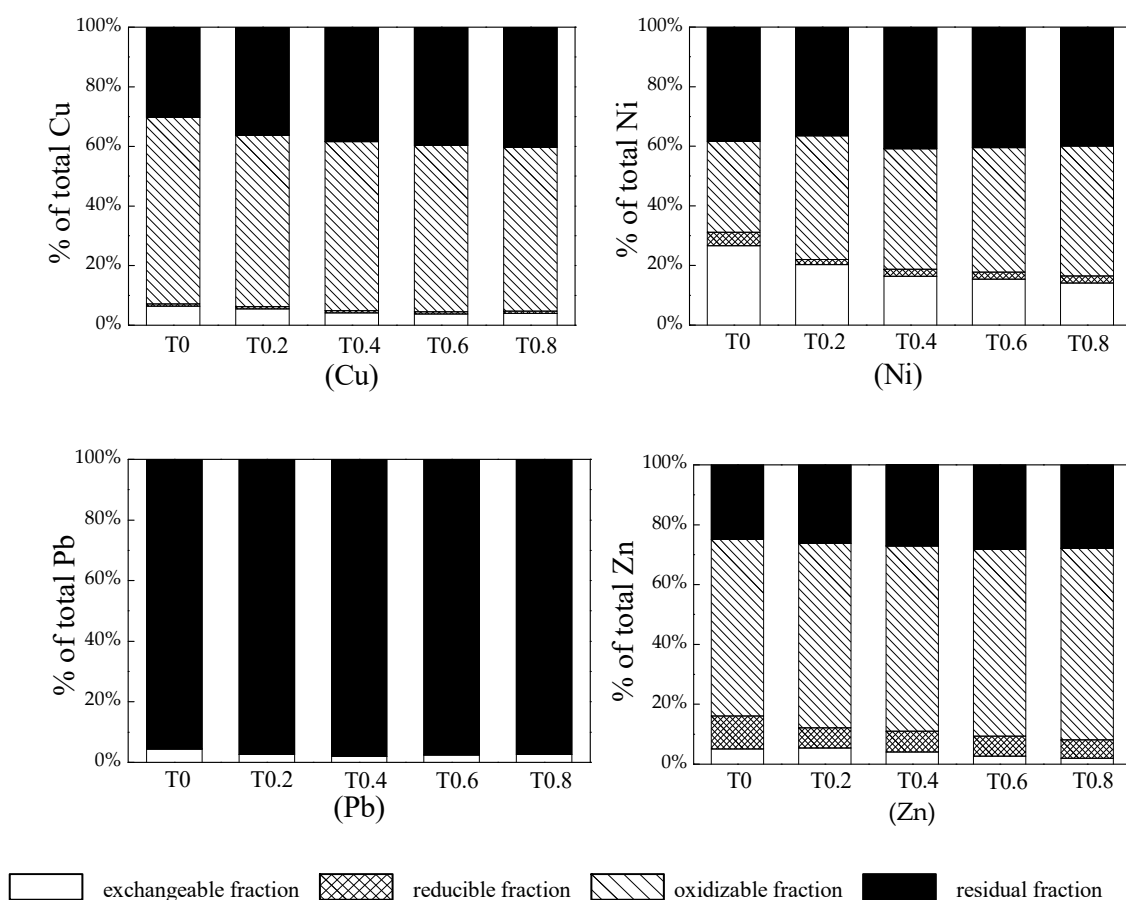
Figure 3. Passivation effect of the TMT on the heavy metals in the sewage sludge.

The exchangeable Pb reduced from 4.42% to 1.99%, and the residual Pb increased from 95.58% to 98.01% when the TMT addition was 0.4%. The immobilization effect of the TMT on Pb was similar to that of the fly ash.

The exchangeable Zn and the reducible Zn reduced, while the residual Zn and the oxidizable Zn increased by adding the TMT. When the TMT addition exceeded 0.6%, there was no obvious enhancement on the Zn immobilization.

By adding 0.6% TMT, the residual Cu, the oxidizable Ni, and the oxidizable Zn increased 31.07%, 36.69%, and 9.33%, respectively, and the exchangeable Cu, the exchangeable Ni, the exchangeable Pb, and the exchangeable Zn reduced by 41.10%, 42.07%, 45.07%, and 48.02%, respectively. Based on the comprehensive immobilizing effect of the TMT on the selected four heavy metals, the optimum dosage of the TMT was determined to be 0.4–0.6%. The immobilization effect of the TMT on Cu was obvious. The exchangeable Cu and the oxidizable Cu were transformed into residual Cu, which was consistent with the result of Pan et al. [53]. However, its immobilization effect on Ni and Zn was not satisfactory, mainly due to the conversion of the exchangeable fraction and the reducible fraction to an oxidizable fraction rather than the residual state.

3.4. Synergistic Passivation of the Fly Ash and TMT

3.4.1. Synergistic Passivation Effect on the Heavy Metals

The addition of the fly ash increased the pH value and helped to form insoluble precipitation, while the TMT immobilized the heavy metals by forming chelate precipitation. Their synergistic passivation effect on the heavy metals is shown in Table 3. The Δresidual fractions of Cu, Ni, and Pb in F20T0.5 were 2.56%, 1.88%, and 0.4% higher than those in F20, respectively. The Δexchangeable

fractions of Cu, Ni, Pb, and Zn in F20T0.5 were 2.18%, 9.5%, 0.4%, and 0.57% higher than those in F20, respectively. These results indicated that the passivation effects of the TMT + fly ash on Cu, Pb, Ni, and Zn were better than those of the fly ash alone. The Δresidual fractions and Δexchangeable fractions of Cu, Ni, and Pb were positive, indicating that good fixation for Cu, Ni, and Pb could be obtained by the fly ash and the fly ash + TMT. The Δresidual fraction of Zn was negative, showing that the passivation effect on Zn was not satisfactory. Further research on Zn fixation must be carried out in the future.

Table 3. Synergistic passivation effect of fly ash + TMT on the heavy metals.

Samples	ΔResidual Fraction				ΔExchangeable Fraction			
	Cu	Ni	Pb	Zn	Cu	Ni	Pb	Zn
F20	16.39	7.34	2.24	−4.94	0.99	3.14	2.24	3.01
F20T0.5	18.95	9.22	2.64	−3.66	3.17	12.64	2.64	3.58

F20: sewage sludge treated by 20% fly ash; F20T0.5: sewage sludge treated by 20% fly ash and by 0.5% TMT.

3.4.2. Effect of the Sewage Sludge on the Ryegrass Growth

The effects of the three treatments on ryegrass growth are shown in Figure 4. The application of sewage sludge significantly increased the plant height, the number of tillers, the chlorophyll content, and the biomass of the ryegrass over the control treatment. The respective increases of 172% and 377% in plant height and 215% and 380% in the number of tillers were observed in the USS treatment and the SSS treatment, respectively. The fresh weight increased from 70.98 mg/m^2 to 786.17 mg/m^2 in the USS treatment and 2349.25 mg/m^2 in the SSS treatment, respectively. The dry weight increased from 15.35 mg/m^2 to 118.44 mg/m^2 in the USS treatment and 291.27 mg/m^2 in the SSS treatment, respectively. These increases were due to the supply of OM and the release of N, P, and micronutrients from the sewage sludge. Many investigators have reported a substantial increase in plant growth and biomass production upon the addition of sewage sludge. Latare reported the same result—that the application of sewage sludge increased the plant height, the number of tillers, and the accumulated aboveground dry matter [6]. Tamrabet et al. indicated that 30 t/ha of sewage sludge was as efficient as 66 kg/ha of mineral nitrogen [54].
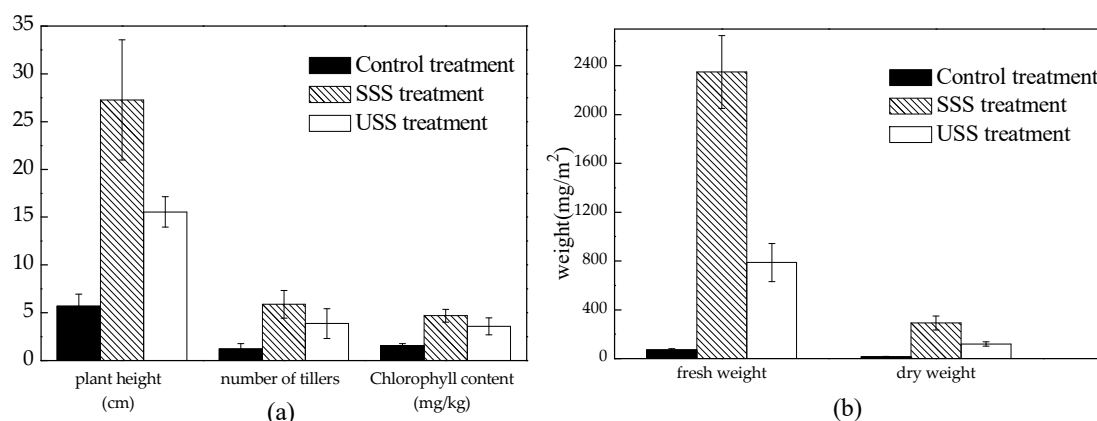

Figure 4. The effects of sewage sludge on ryegrass growth. (**a**) the effect on the plant height, the number of tillers, and the chlorophyll content; and (**b**) the effect on fresh weight and dry weight.

The present study indicated that the addition of sewage sludge also increased the chlorophyll content. Chlorophyll is the molecule that performs photosynthesis in the chloroplasts of green plants. Changes in chlorophyll content could occur as a result of nutrient deficiencies or exposure to environmental stress [55]. Bilgili and Acikgoz pointed out that turf color and quality are associated with N fertility treatments and that increasing nitrogen significantly enhanced the color and quality ratings of several turfs [56]. The chlorophyll content in the control treatment was the lowest among

the three treatments, which was mainly attributed to the low content of N in the brown soil. The high chlorophyll contents in the USS and SSS treatments were mainly ascribed to the supplement of N nutrient from the sewage sludge.

The adverse effect of the heavy metals in the sewage sludge on the ryegrass growth was alleviated by the passivation of the fly ash and TMT, which led to the higher levels of plant production and chlorophyll content in the SSS treatment than in the USS treatment. The plant growth, number of tillers, chlorophyll content, fresh weight, and dry weight in the SSS treatment increased 77.6%, 52.4%, 30.6%, 199%, and 146%, respectively. These results were indicative of the fertilizer effect of the addition of the sewage sludge on the ryegrass growth, as well as the stress of the heavy metals on the ryegrass growth with the addition of 20% sewage sludge.

3.5. Passivation Mechanism of the Fly Ash and TMT on the Heavy Metals

Fly ash mainly consists of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, and so on. The alkaline materials, such as CaO and MgO, are beneficial to the formation of the iron–manganese bound state and the residual state, and iron oxides can combine with heavy metals to form the iron–manganese bound state. The pH value of the sewage sludge immobilized by the fly ash increased, while the EC decreased with the increasing addition of the fly ash (Figure 5). The pH value of the fly ash was 10.88, which was far higher than that of the sewage sludge (6.89). The high pH was beneficial for the heavy metals to form insoluble precipitation, which transformed part of the heavy metal ions into the residual fraction. The decrease of the EC was partly due to the addition of the fly ash with low EC into the sewage sludge. On the other hand, the precipitation of the exchangeable metals was another reason for the reduction of the EC. A similar result indicated by Zhang et al. demonstrated that the treatment with fly ash stabilized Pb and Cd effectively [57].
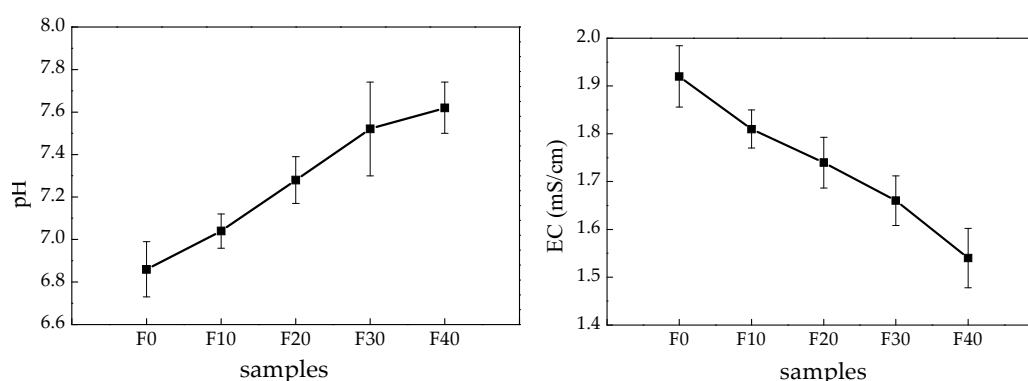

Figure 5. Effect of the addition of fly ash on the pH and EC.

The XRD patterns of the fly ash and the treated and untreated sewage sludge were recorded in Figure 6 and analyzed by Jade software. The results showed that the main crystal phases in the fly ash were SiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$, and CaO (Figure 6a). The sewage sludge was a multi-phase system consisting of many kinds of organic and inorganic substances, many of which existed in amorphous form. Its pattern consisted of strong intensity peaks corresponding to SiO_2 and weak peaks of $Pb(NO_3)_2$, $CuCl_2 \cdot 2H_2O$, $Ca_2Cu(SO_4)_3 \cdot 2H_2O$, $CaZn(CO_3)_2$, $Zn(NO_3)_2 \cdot 2H_2O$, $NiCl_2 \cdot 4H_2O$, and $NiSO_4$ (Figure 6b). The addition of the fly ash was beneficial to the formation of the insoluble basic salts (such as $Pb_3(NO_3)(OH)_5$, $Cu_3(SO_4)(OH)_4$, $Zn_5(NO_3)_2(OH)_8 \cdot 2H_2O$, $Cu_2Cl(OH)_3$, $Ni_2Cl(OH)_3$, and $CaZn(CO_3)(OH)_2$) and metal hydroxides such as $Ni(OH)_2$ and $ZnSO_4 \cdot 2Zn(OH)_2$ (Figure 6c). The reduction of the exchangeable fraction in the treated sewage sludge might be attributed to the transformation of the heavy metals from soluble salts to insoluble basic salts. Masto et al. indicated that the pH increase caused the precipitation of heavy metals in the treated sewage sludge, which was the most influential factor that caused the reduction in diethylenetriaminepentaacetic acid (DTPA)-extractable Zn, Co, and Cu [58].
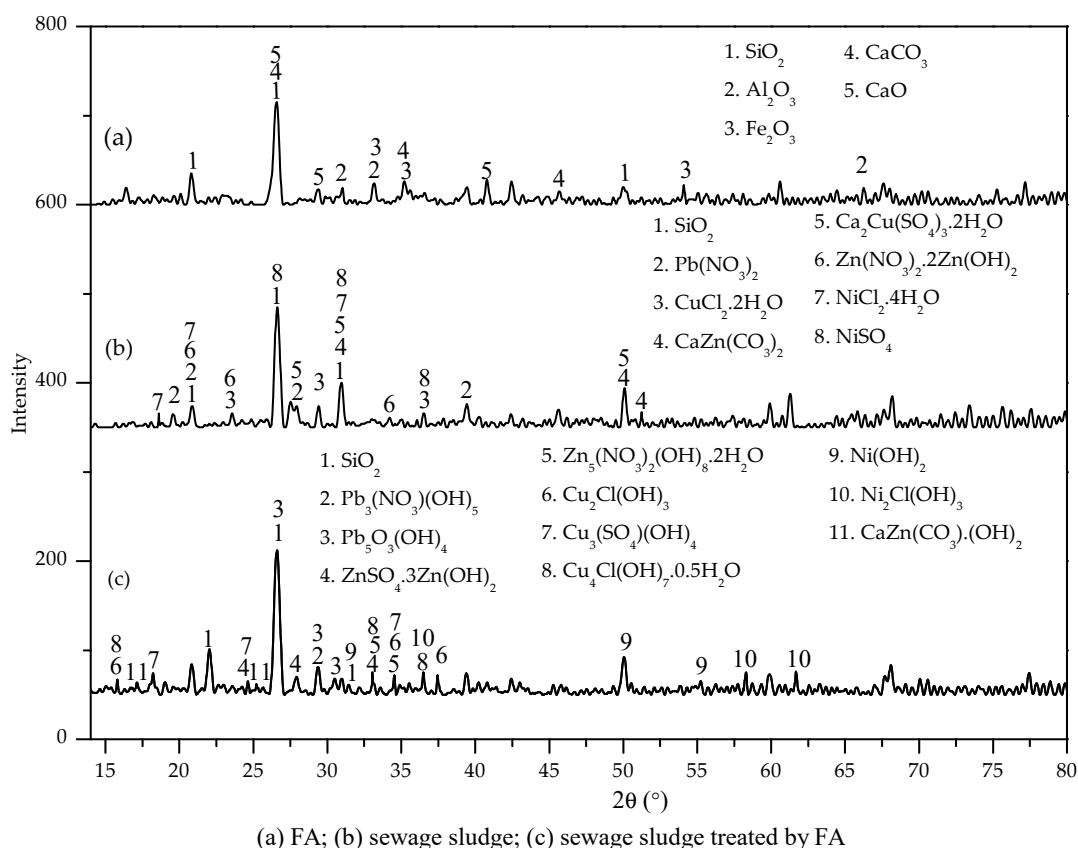
(a) FA; (b) sewage sludge; (c) sewage sludge treated by FA

Figure 6. XRD diagrams of the fly ash and the sewage sludge.

In addition, fly ash generally possesses many desirable capabilities, such as adsorption, ion exchange, coagulability, and precipitability and shows high performance with respect to heavy metal passivation. Xu et al. indicated that high specific surface areas and small pore diameters were beneficial for removing mercury efficiently [48]. The CEC of the used fly ash was as high as 79.59 ± 2.06 mmol/kg, and its specific surface area was only 2.09 m^2/g, which was similar to that of the sewage sludge (2.03 m^2/g). This indicated that the immobilization performance of the fly ash was mainly due to the formation of precipitation under high pH conditions and ion exchange rather than adsorption.

The TMT was added into the sewage sludge immobilized by the fly ash to improve the immobilization performance. Its special sulfur group could combine with heavy metals by chelate precipitation. In aqueous solutions, the TMT existed mainly in four forms: $(C_3N_3S_3)^{3-}$, $(HC_3N_3S_3)^{2-}$, $(H_2C_3N_3S_3)^-$, and $(H_3C_3N_3S_3)^0$. The main form was determined by the pH value of the solution. In the SSS treatment, the pH value was 7.28 and $(H_2C_3N_3S_3)^-$ was the main form reacting with the heavy metal ions and forming chelating precipitates according to Equation (1) and Equation (2).

$$(H_2C_3N_3S_3)^- + M^+ \rightarrow MH_2C_3N_3S_3 \downarrow . \tag{1}$$

$$2(H_2C_3N_3S_3)^- + M^{2+} \rightarrow M(H_2C_3N_3S_3)_2 \downarrow . \tag{2}$$
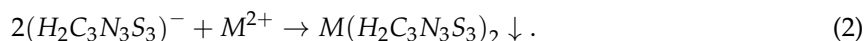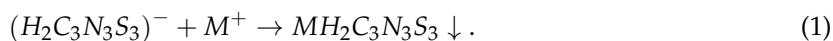
Figure 7 shows the SEM images of the brown soil, the sewage sludge, the fly ash, and the immobilized sewage sludge. The brown soil sample showed a single granular structure rather than a cluster structure (Figure 7a), meaning the degree of the brown soil agglomeration was very low, which might have been due to the low content of OM. Its OM content was only 17.87 g/kg, which was lower than the average OM content in Chinese plough layer (24.65 g/kg) [59]. The low content of OM indicated that the soil fertility in the study area was low, and the addition of OM would help to improve this condition. Figure 7b shows that the sewage sludge particles were dispersive, with

irregular structures, such as lumps and flakes. Their sizes varied greatly. During the air drying process of the dewatered sludge, with the migration and diffusion of the inner water, the sludge produced cracks, shrinkage, and agglomeration, and its hardness increased [60]. The air-dried sludge was crushed by mechanical force to obtain irregular particles that had folded surfaces. The fly ash particles were mainly spherical in shape and consisted of solid spheres, hollow microspheres, irregular-shaped debris, and porous unburnt carbon (Figure 7c). Its compact surface resulted in a low specific surface area (2.09 m^2/g) and was not conducive to the passivation of heavy metals through adsorption. The SEM images of the sewage sludge treated by the fly ash showed that the fly ash was mixed loosely with the sewage sludge (Figure 7(d1,d2)). In the sewage sludge treated by the fly ash + TMT (Figure 7(e1,e2)), the fly ash particles were wrapped by sludge particles, and they were fully contacted and formed some more compact microstructures, which were conducive to ion exchange between the heavy metals in the sewage sludge and in the fly ash. Thus, the TMT not only formed chelating precipitates with the heavy metals but could also help the treated sewage sludge to form a dense structure, which could improve the immobilization of the heavy metals. The synergistic effect of the fly ash and TMT could improve the passivation effect on the heavy metals in the sewage sludge.
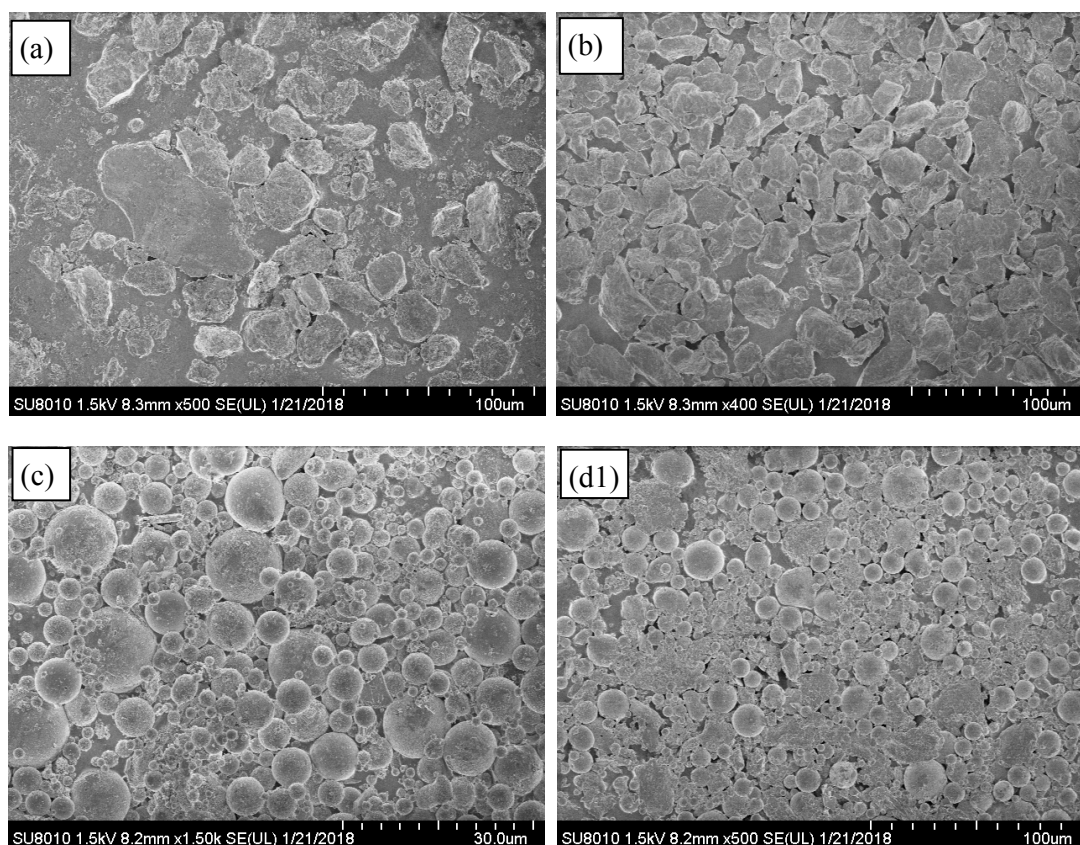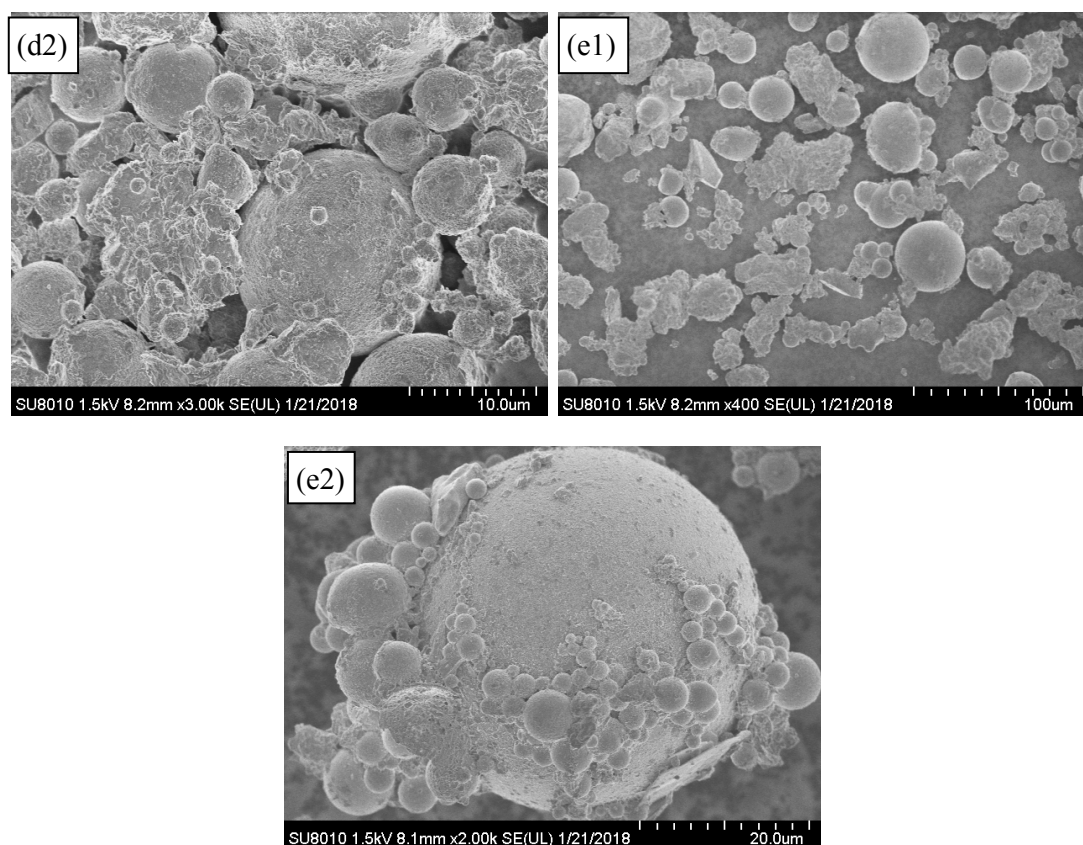

Figure 7. *Cont.*

Figure 7. SEM images of the soil, the fly ash, and the sewage sludge. (**a**) the brown soil; (**b**) the sewage sludge; (**c**) the fly ash; (**d1**) and (**d2**) the sewage sludge treated by the fly ash; and (**e1**) and (**e2**) the sewage sludge treated by the fly ash + TMT.

4. Conclusions

TMT and fly ash were synergistically used to passivate heavy metals in sewage sludge in order to improve the fixation effect, which would help to solve the obstacle restraining the land application of sewage sludge and to realize the resource utilization of fly ash.

The selected dewatered sewage sludge was rich in OM, N, and P, which satisfied the nutritional demand of GB/T23486-2009. The contents of the four heavy metals (Cu, Ni, Zn, and Pb) were below the limits of GB/T23486-2009. Fly ash and TMT was used to stabilize the heavy metals in the sewage sludge and showed different passivation effects on the four selected heavy metals. The optimum effect could be gained by adding 10–20% fly ash or 0.4–0.6% TMT. Their synergistic passivation of 20% fly ash +0.5% TMT was superior to adding the fly ash alone. The plant height, the tiller number, and the chlorophyll content increased by 172%, 215%, and 126% in USS treatment and by 377%, 380%, and 196% in the SSS treatment, respectively. The fresh weight and dry weight were 6.7 and 10.1 times higher in USS treatment and 32.1 and 18.0 times higher in the SSS treatment, respectively. The adverse effect of the heavy metals in the sewage sludge on the ryegrass growth could be alleviated by the synergistic passivation of fly ash + TMT. The immobilization performance of the used fly ash was mainly due to the formation of precipitation under high pH conditions and ion exchange, while the effect of TMT was due to chelate precipitation.

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