REMEDIATION OF MICROPALSTIC-HEAVY METAL CO-CONTAMINATED SOILS USING NANOSCALE ZERO-VALENT IRON SUPPORTED ON PALYGORSKITE: MECHANISMS AND EFFECTIVENESS

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Abstract. This study investigates the remediation of microplastic-heavy metal co-contaminated soils using nanoscale zero-valent iron (nZVI) supported on palygorskite (PAL), referred to as PAL-nZVI. The composite material was successfully synthesized via a co-precipitation method and characterized using SEM, XRD, and FTIR. The results demonstrated that PAL-nZVI effectively inhibited the migration of microplastics in soil, with the microplastic content in the 10-15 cm layer remaining at only 8.42% of the initial amount after 28 days of treatment with 1% PAL-nZVI, compared to 15.59% in the control group. Additionally, PAL-nZVI significantly enhanced the stabilization of heavy metals, reducing the bioavailable fractions of cadmium (Cd) and lead (Pb). The weak acid-extractable fraction of Cd decreased by 11.55%, while the residual fraction increased by 11.46%. For Pb, the oxidizable fraction decreased by 22.34%, and the residual fraction increased by 27.35%. The potential ecological risk index (RI) for Cd and Pb decreased by 55.53% and 79.86%, respectively, with 2% PAL-nZVI treatment. The remediation mechanisms included physical adsorption, chemical reduction, surface complexation, and ion exchange. PAL-nZVI's high specific surface area and functional groups facilitated the adsorption of microplastics and heavy metals, while the reducibility of nZVI transformed high-valence heavy metal ions into low-valence states, reducing their toxicity. This study provides a promising approach for the remediation of soils co-contaminated with microplastics and heavy metals. However, further research is needed to optimize the process and evaluate long-term environmental impacts.
Keywords: *nanoscale zero-valent iron, palygorskite, microplastic, heavy metal, soil*

Introduction

In recent years, plastic products have been widely used worldwide because of their low cost, excellent performance, and versatility (Piccardo et al., 2020; Zhao et al., 2024). However, these plastic products will gradually break down and decompose after physical, chemical, and biological effects in the environment, forming microplastics with a particle size of less than 5 mm (MPs) (Wang et al., 2022; Dhevagi et al., 2024). According to statistics, millions of tons of microplastics enter the environment every year, and soil, as an essential environmental medium, has become a vast "reservoir" of microplastics (Xu et al., 2020; Chang et al., 2022). In agricultural production, the extensive use of plastic films, drip irrigation tubes, and other agricultural plastic products, as well as sewage irrigation, sludge farming, and other activities, make microplastics continue to accumulate in the soil (Liu et al., 2024; Zhang et al., 2025). At the same time, the problem of soil heavy metal pollution is also severe. Mining, smelting, electroplating, and other industrial activities will release a large amount of wastewater, waste gas, and waste residue containing heavy metals into the environment, and these heavy metals will eventually enter the soil through atmospheric deposition, surface runoff, and other ways (Qin et al., 2021; Singh et al., 2025). In the field of agriculture, the long-term irrational

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use of chemical fertilizers, pesticides, livestock and poultry manure, etc., will also lead to soil heavy metals such as cadmium (Cd), lead (Pb), mercury (Hg) exceed the standard (Xu et al., 2021). For example, some phosphate fertilizers contain relatively high concentrations of cadmium, and long-term application will cause soil cadmium pollution (Ghuge et al., 2023).

The situation becomes more complicated when microplastics coexist with heavy metals in the soil (Wang et al., 2021; Zhao et al., 2023). Microplastics have a large specific surface area and rich surface charge, which can adsorb heavy metal ions in soil and change their migration and transformation law (Guo et al., 2020; Yu et al., 2021). On the one hand, microplastics may act as carriers to promote the migration of heavy metals in soil, making it easier to enter groundwater or be absorbed by plants, thereby increasing the bioavailability and environmental risks of heavy metals (Abbasi et al., 2020; Xiang et al., 2022; Wang et al., 2025). On the other hand, microplastics may change soil's physical and chemical properties, such as soil aggregate structure, porosity, pH, etc., and then affect the adsorption-desorption equilibrium and morphological distribution of heavy metals in soil (Li et al., 2019). Heavy metals may also interact with microplastics, changing their surface properties and biodegradability and enhancing their environmental toxicity (Khalid et al., 2021). For example, some heavy metal ions may react with functional groups on the surface of microplastics, making it more difficult for microplastics to be degraded by microorganisms. This combined microplastic-heavy metal pollution significantly threatens soil ecosystems and human health (Song et al., 2023). In the soil ecosystem, combined pollution can affect the community structure and function of soil microorganisms, inhibit soil enzyme activity, and reduce soil fertility and self-purification ability (Jia et al., 2022). For plants, combined pollution may hinder the growth and development of plant roots, affect the absorption of nutrients and water by plants, and reduce the yield and quality of crops (Zhang et al., 2023). What is more serious is that through the transmission and enrichment of the food chain, these pollutants may eventually enter the human body, causing damage to the human nervous system, immune system, reproductive system, and so on.

Nano-ferric zero-valent (nZVI) has attracted extensive attention in soil remediation because of its high specific surface area, strong reducibility, and good adsorption properties (Fajardo et al., 2019). The nano zero-valent iron can reduce the high metal ions to the low metal ions through reduction and reduce their toxicity and migration (Xue et al., 2018). At the same time, it can also react with some organic pollutants and promote their degradation (Yan et al., 2013). However, some problems in the practical application of nano-zero-valent iron, such as easy aggregation and poor stability, affect its repair effect and service life (Arancibia-Miranda et al., 2016). Palygorskite (PAL) is a clay mineral with a fibrous crystal structure, unique pore structure, and large specific surface area (Zhang et al., 2025). It is rich in various active groups on the surface. It has a good adsorption capacity for heavy metal ions and can fix heavy metals on its surface through ion exchange and surface complexation (Zotiadis et al., 2012). In addition, PAL also has the advantages of low cost, abundant reserves, and environmental friendliness. It is expected that a composite material with excellent properties can be prepared by loading nano-zero-valent iron onto the surface of PAL, which not only takes advantage of the strong reducibility and high activity of nano-zero-valent iron but also takes advantage of the adsorption property and stable structure of PAL to overcome the agglomeration problem of nano-zero-valent iron and improve its stability and effectiveness in soil remediation (Xu et al., 2019).

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The problem of microplastic-heavy metal composite pollution of soil is increasingly prominent, but the remediation technology for this composite pollution is still relatively scarce. Developing efficient, green, and sustainable remediation technologies to treat soil contaminated by microplastics and heavy metals has become a hot research topic and an urgent problem in environmental science. Therefore, the main objectives of this study are as follows: 1) Using the co-precipitation method to uniformly and stably load nano-zero-valent iron (nZVI) onto palygorksike (PAL) surface to prepare high-activity and high-stability nano-zero-valent iron loaded palygorksike (PAL-nZVI) composite; 2) Comprehensive assessment of the remediation effect. By setting multiple groups of controlled experiments, a systematic study was conducted on the remediation effect of different doses of PAL-nZVI on the soil contaminated by microplastics and heavy metals. Advanced analytical techniques were used to comprehensively detect the mobility of microplastics in the soil and the changes in the bioavailability and morphological distribution of heavy metals. Quantitative evaluation of PAL-nZVI 's ability to remove and stabilize complex pollutants; 3) In-depth analysis of the mechanism of action: With the help of scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR) and other characterization methods, the interaction mechanism between PAL-nZVI and microplastics and heavy metals was deeply explored from the microscopic level. Based on the experimental results, the feasibility and potential value of PAL-nZVI in actual soil remediation were evaluated, providing a theoretical basis and practical guidance for the development of economical, efficient, and environmentally friendly microplastics-heavy metal composite remediation technology.

Materials and methods

Experimental material

Palygorskite (PAL) was purchased from Xuyu, Jiangsu Province. Its purity has been tested to reach more than 95%. It has a fibrous crystal structure and a specific surface area of about 150-200 m^2/g. The nano zero-valent iron (nZVI) was prepared using liquid phase reduction. The reagents used in the test, ferrous sulfate ($FeSO_4 \cdot 7H_2O$, AR) and Sodium Borohydride ($NaBH_4$, AR), were purchased from Sinopsin Chemical Reagents Co., LTD. Microplastics select polyethylene (PE) microplastic particles in 100-500 μm size range, supplied by Huayu Co., Ltd. (Guangzhou, China). Cadmium (Cd) and lead (Pb) were selected as heavy metals. The pure reagents were analyzed with 99.9% cadmium nitrate (Cd $(NO)_2$ $4H_2O$, AR) and lead nitrate (Pb $(NO)_2$, AR), respectively, and solutions of different concentrations were prepared to simulate pollution. The experimental soil was collected from a typical farmland in Anning District (103◦43′52″E, 36◦6′48″N), Lanzhou City, Gansu Province. The soil type of this farmland was lime-calcic soil, and the collection depth was 0-20 cm. The physicochemical properties of the soil were as follows: pH of 6.42, organic matter content of 1.37%, total nitrogen (N) content of 1.25 g/kg, total phosphorus (P) content of 0.46 g/kg, Pb^{2+} concentration of 17.6 mg/kg, and Cd^{2+} concentration of 0.04 mg/kg. The collected soil was naturally air-dried to remove impurities such as plant residues and stones, then ground with agate mortar and passed through a 2 mm nylon screen for reserve use.

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Synthesis of PAL-nZVI

Weigh 5 g palygorskite powder, add it to 200 mL deionized water, and place it in an ultrasonic cleaner and ultrasonic treatment at 40 kHz for 30 min to thoroughly disperse to form a uniform suspension. A mixed solution containing Fe^{2+} and Fe^{3+} (a molar ratio of 2:1), in which the combined concentration of Fe^{2+} and Fe^{3+} is 0.5 mol/L, is added slowly to a palygorskite suspension with a drop acceleration controlled at 1-2 drops/second, agitated by a magnetic agitator. After the drip, the pH value of the reaction system was adjusted to 10-11 with 1 mol/L sodium hydroxide (NaOH) solution. Then, the sodium borohydride solution with a concentration of 0.1 mol/L was added drop by drop with an acceleration of 0.5-1 drops/second while maintaining the stirring state. During the reaction process, the color of the solution gradually changed from light yellow to black, indicating that nano zero-valent iron began to form and be loaded on the surface of palygorskite. After the reaction lasted for one hour, the agitation was stopped, the reaction liquid was transferred to the centrifuge tube, centrifuged at 8000 r/min for 10 min, and the supernatant was discarded. Repeated washing of precipitation with deionized water and anhydrous ethanol 3-5 times to remove residual impurities and unreacted reagents on the surface. Finally, the washed product was placed in a freeze-dryer and dried at -50 ℃ and vacuum degree of 10^{-3} mbar for 24 h to obtain a nano-ferric zero-valence loaded palygorskite (PAL-nZVI) composite.

Soil pollution simulation and remediation experiment

According to the previous investigation data of contaminated soil, the proportion of microplastics and heavy metals added was determined (De Souza Machado et al., 2019; Yu et al., 2021). A certain amount of PE microplastic particles was weighed and added to 1 kg of sifted soil at a ratio of 5 g/kg. At the same time, cadmium nitrate and lead nitrate solutions were added to the soil so that the initial content of cadmium and lead reached 5 mg/kg and 100 mg/kg, respectively. The soil added with microplastics and heavy metals was placed in a rotating mixer and mixed for two hours at 100 r/min to ensure the uniform distribution of pollutants. The simulation of microplastic-heavy metal composite contaminated soil was obtained. The control group (CK) and three experimental groups (T1, T2, T3) were set up, with three replicates in each group. The control group did not add repair material; the experimental group added 0.5%, 1%, and 2% (mass fraction) PAL-nZVI composite material, respectively. The remediation materials were thoroughly mixed with the composite contaminated soil, and deionized water was added to adjust the soil water content to 60% of the field water capacity by controlling the watering frequency and watering volume. The mixed soil is placed in a plastic bowl, covered with plastic wrap, pierced with several small holes in the plastic wrap to ensure ventilation, and then placed in a constant temperature incubator at 25℃. Soil samples were collected on the 7th, 14th, 21st, and 28th days after culture, and about 300 g were collected for each sample to analyze the content and morphological changes of microplastics and heavy metals.

Analytical method

The microstructure and morphology of PAL-nZVI were observed by scanning electron microscope (SEM) (JSM-7610F, Nippon Electronics Co., LTD) under 15 kV acceleration voltage. After gold spraying, the sample is fixed on the sample table for testing. The crystal structure was analyzed by the X-ray diffractometer (XRD) (D/MAX-2500, Rigaku Co., LTD.). The test conditions were as follows: Cu target Kα radiation, tube voltage

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40 kV, tube current 100 mA, scanning range 2θ = 5°-80 °, and scanning speed 8°/min. The changes of surface functional groups were detected by Fourier transform infrared spectrometer (FTIR) (Nicolet iS50, Thermo Fisher Technology Co., LTD.). The samples were mixed with KBr and then scanned in the wave-number range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

The separation of microplastics in soil is done by density flotation. The collected soil sample was placed in a 500 mL glass beaker, adding an appropriate amount of saturated sodium chloride solution (density of about 1.2 g/cm^3), stirring for 30 min at a speed of 150 r/min so that the microplastics and soil particles were entirely separated. The suspension is then transferred to the separation funnel and stratified for one hour so that the microplastics float on the upper layer of the solution. Use a straw to carefully absorb the microplastic solution in the upper layer and transfer it to another glass container. Repeat the above procedure 3-4 times to ensure that the microplastics are entirely separated. The separated microplastics are washed repeatedly with deionized water to remove the residual salt on the surface. A microscope (Zeiss Axio Imager A2m) was used for microscopic imaging to observe the form and quantity of microplastics, and FTIR (Nicolet 6700, USA) was used to analyze the isolated microplastics by infrared spectroscopy to determine their content.

The heavy metal content was determined by an inductively coupled plasma mass spectrometer (ICP-MS) (iCAP Q, Thermo Fisher Technologies, USA). After the soil samples were digested by the nitric acid-hydrofluoric acid-perchloric acid digestion system, the volume was fixed into a 50 mL volumetric bottle. Then, the machine was used for determination. The Bureau of Community Relations sequential extraction procedure (BCR) was used to analyze the heavy metal morphology, and heavy metals were divided into four forms: exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4). Different extractants were used to extract the heavy metals in the extraction solution. ICP-MS was also used to determine the heavy metal content.

Statistical analysis

The calculation method of soil heavy metal stability quotient (SQ) is:

$$SQ=\frac{F_1+F_2+F_3}{F_4}\times 100\% \qquad \text{(Eq.1)}$$

Among them, F1, F2, F3 and F4 represent the contents of a certain heavy metal exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction (mg/kg).

The calculation method of soil heavy metal stabilization rate (RR) is:

$$RR=\frac{F_4}{F_1+F_2+F_3+F_4}\times 100\% \qquad \text{(Eq.2)}$$

Among them, F1, F2, F3 and F4 represent the contents of a certain heavy metal exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction (mg/kg).

The calculation method of soil heavy metal potential ecological hazard index (RI) is:

$$RI=\mathrm{T}\times \frac{C_{soil}}{C_{background}} \qquad \text{(Eq.3)}$$

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Among them, T is the toxic response coefficient, and different heavy metals take different values according to their toxicity intensity. T_{Cd} = 30, T_{Pb} = 5; C_{soil} is the content of heavy metal in the soil; $C_{background}$ is the soil background reference value of heavy metal, Cd = 0.45 mg/kg, Pb = 250 mg/kg.

The data obtained in this research institute is processed and drawn using Microsoft Office 2010 and Origin Pro 9.1 (Windows version). SPSS 2018 (Windows version) and ggplot2 package in R language were used for statistical data analysis, and one-way ANOVA, Duncan tests, and Pearson Correlation Coefficient were used to respond to the significance differences and correlations between different indicators.

Results and discussion

Characterization of PAL-nZVI

It can be seen from *Figure 1a, b* that due to the influence of magnetism and van der Waals forces, the exposed nZVI showed apparent agglomeration and a chain structure; after the nZVI loaded with PAL, a large number of spherical nanoparticles with particle sizes of 50-100 nm were evenly distributed on the PAL-nZVI surface. These nanoparticles were closely attached to the surface of the abrasive fibers, forming a rough and porous structure, which significantly increased the specific surface area of the composite. The surface groups of PAL, nZVI, and PAL-nZVI are characterized by FTIR spectra (*Figure 1c*). The characteristic peaks of PAL are mainly distributed in 4000-3000 cm^{-1} and 1200-400 cm^{-1}. The former is primarily caused by moisture inside PAL and Si-OH, Al-OH, and Mg-OH, while the latter is caused by the vibration of the skeleton of PAL clay (Xu et al., 2019). PAL-nZVI showed a -OH tensile vibration peak at 3348 cm^{-1}, indicating a hydrogen-oxygen bond between PAL and nZVI, and Si-OH and Fe-OH are present on the PAL-nZVI surface. The characteristic peak of nZVI at 3440 cm^{-1} is due to the formation of FeOOH on the nZVI surface (Su et al., 2016). The characteristic peaks at 1033, 777, and 540 cm^{-1} may result from stretching and deformation vibrations of Si-O-Si and Al-O-Si in PAL. It can be seen that a large number of functional groups, such as -OH, Fe-O, and FeOOH, are generated on the surface of PAL-nZVI, providing a large number of active sites for the complexation of heavy metals. Among the many functional groups, oxygen-containing functional groups play a vital role in the stability of heavy metals (Liu et al., 2020). The XRD spectrum of PAL, nZVI, and PAL-nZVI is shown in *Figure 1d*. The diffraction peaks with 2θ of 8.49, 22.9, 26.7, 30.97, and 43.44 are characteristic peaks of PAL (Chen et al., 2018). The diffraction peak with 2θ of 44.9° is the characteristic peak of α-Fe0 (Chen et al., 2018; Zhang et al., 2019). The diffraction peak with 2θ of 29.5° is the characteristic peak of FeO(OH). After the nZVI is loaded with PAL, the typical characteristic peaks of PAL and nZVI are retained in the XRD pattern of PAL-nZVI, indicating that nZVI was successfully loaded on the PAL surface, while the crystal structure of PAL did not change.

Effects of PAL-nZVI on soil physicochemical properties

When PAL-nZVI was added to repair the soil contaminated by microplastics and heavy metals, the physical and chemical properties of the soil changed significantly. The experimental results show that the pH value of the soil in the control group remained stable during the culture cycle, maintaining at about 6.55.

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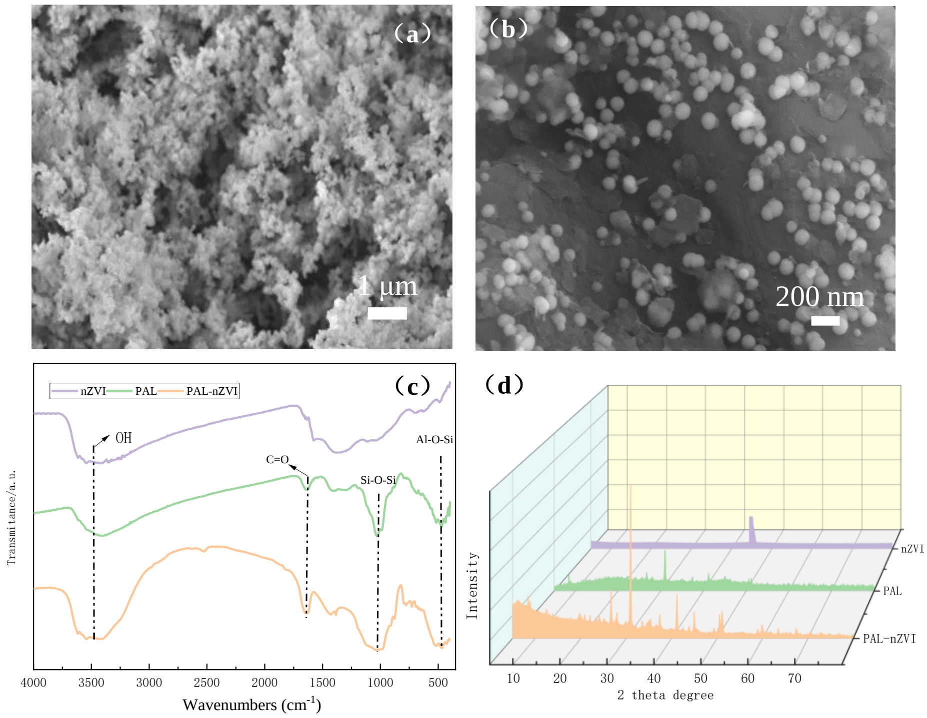

Figure 1. *SEM images of (a) nZVI and (b) PAL-nZVI; (c)FT-IR spectra; (d) XRD patterns*

When PAL-nZVI was added, the soil pH value increased to 7.28 after 28 days of culture when the addition amount was 2% (*Figure 2a*). This is mainly due to the fact that the nano zero-valent iron consumes H^+ in the soil solution during the reaction. At the same time, the alkaline groups on the surface of PAL also play a regulating role in soil pH. In addition, soil cation exchange capacity (CEC) is also affected. After adding PAL-nZVI, soil CEC increased significantly, and the experimental group with 2% PAL-nZVI increased soil CEC by 20.81% compared with the control group (*Figure 2b*). This is mainly due to the high cation exchangeability of PAL itself, and the exchange reaction between the functional groups on the surface of PAL-nZVI and the cations in the soil increases the adsorption and exchangeability of the soil. Regarding soil porosity, with the increase of PAL-nZVI addition, soil porosity showed a trend of first increasing and then decreasing. When the addition amount was 1%, the soil porosity reached the maximum value, which was increased by 14.86% compared with the control group (*Figure 2c*). This is because adding PAL-nZVI promotes the formation of soil aggregates, rearranges soil particles, and increases the number of macropores. However, when the amount of PAL-nZVI added is 2%, excess nanoparticles may fill the soil pores, resulting in a slight decrease in porosity.

Soil enzyme activity is an important index to measure soil fertility and ecological function. The addition of heavy metals and microplastics to soil can affect the denitrification of soil, the growth of nitrogen-fixing bacteria, and the content of available phosphate in soil, improve the storage and cycling efficiency of soil nitrogen, and then affect the activity of soil urease and phosphatase (Li et al., 2024). This study investigated the effects of PAL-nZVI on soil urease, catalase, and phosphatase activities. Experimental data showed that in the control group, due to microplastics-heavy metal composite contamination, soil urea enzyme activity was 212.61 μmol/d/g at the beginning of culture

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and decreased to 186.85 μmol/d/g by 28 days of culture over time (*Figure 3a*). The results showed that pollution inhibited urease activity in soil nitrogen conversion. After the addition of PAL-nZVI, soil urease activity significantly improved. When added at 1%, the urease activity reached 331.82 μmol/d/g after 28 days of culture, probably because PAL-nZVI improves the soil environment and provides more favorable living conditions for microorganisms involved in the nitrogen cycle, thus promoting urease secretion. The catalase activity in the control soil was relatively stable during culture at around 9.5 μmol/d/g. Upon addition of PAL-nZVI, catalase activity increased to 13.70 μmol/d/g at 28 days of culture when added at 2% (*Figure 3b*). Catalase is involved in the decomposition of hydrogen peroxide in soil, and the improvement of its activity means that the REDOX ability of soil is enhanced, which is conducive to the decomposition and transformation of some harmful substances in soil, which may be related to the REDOX characteristics of PAL-nZVI. Soil acid phosphatase activity was also significantly affected (*Figure 3c*). Soil acid phosphatase activity in the control group was 12.80 μmol/d/g at the initial stage of culture and decreased to 12.23 μmol/d/g after 28 days of culture, reflecting the inhibition of soil phosphorus conversion by combined pollution. After adding PAL-nZVI, soil acid phosphatase activity increased significantly, and the experimental group supplemented with 2% PAL-nZVI reached 15.54 μmol/d/g after 28 days of culture. This suggests that PAL-nZVI helps to promote the decomposition of organophosphorus in soil and improve the availability of phosphorus, possibly because it improves the physical and chemical properties of soil and enhances the mineralization of organophosphorus by microorganisms. In addition, microplastics can increase the water-holding capacity of soil, while the activities of urease and acid phosphatase are sensitive to soil water, and when the water content in soil increases, the activities of urease and acid phosphatase also increase (De Souza Machado et al., 2018). Dehydrogenase is mainly involved in microbial respiration. Adding heavy metals and microplastics changes soil void structure to some extent, enhancing microbial activity and reducing soil O_2, thus enhancing dehydrogenase activity (Fei et al., 2020).

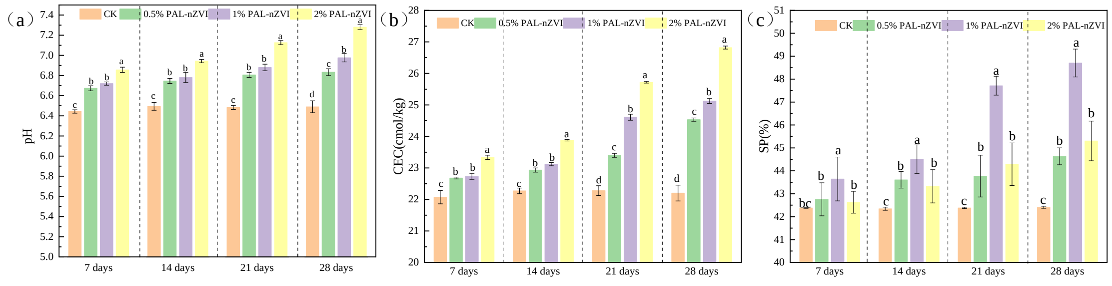

Figure 2. *Impact of various treatment groups on soil pH(a), CEC(b) and SP(c) at different culture times. (Different lowercase letters represent significant difference among each treatment (n = 3, p < 0.05))*

Migration and change of microplastics in soil

In the control group, without adding repair materials, the migration of microplastics in soil was evident with the extension of culture time. The analysis of microplastics in soil samples at different depths showed that after 7 days of culture, the content of microplastics in the surface layer (0-5 cm) was 85.42% of the initial addition amount, while the content of microplastics at 10-15 cm depth was only 4.65% of the initial

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addition amount (*Figure 4*). After 28 days of culture, the content of microplastics in the soil surface decreased to 61.32% of the initial addition amount, while the content of microplastics at 10-15 cm depth increased to 15.89%, indicating that microplastics continued to migrate to the deep soil.

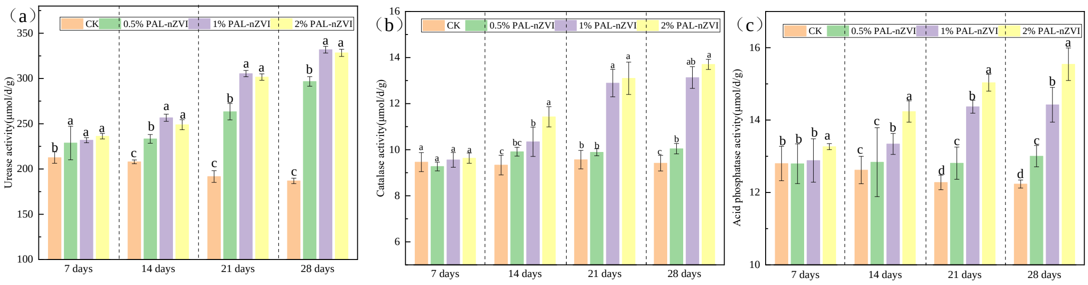

***Figure 3.** Impact of various treatment groups on soil urea enzyme activity (a), catalase activity (b) and acid phosphatase activity (c) at different culture times. (Different lowercase letters represent significant difference among each treatment (n = 3, p < 0.05))*

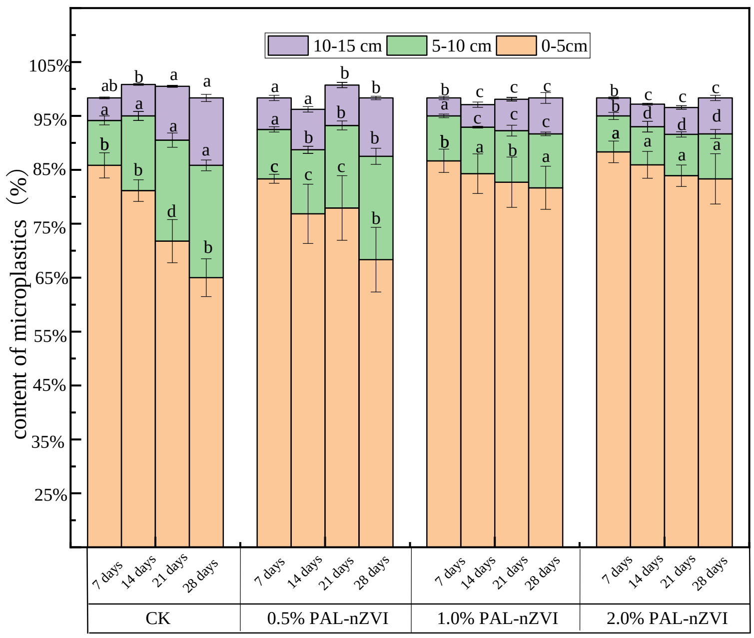

***Figure 4.** Impact of various treatment groups on the content of microplastics at different depths*

When PAL-nZVI was added, the migration of microplastics was significantly inhibited. In the experimental group supplemented with 1% PAL-nZVI, after 28 days of culture, the microplastic content of the soil surface (0-5 cm) remained at about 79.38% of the initial addition amount, and the microplastic content at 10-15 cm depth was only 8.42%. This is mainly because PAL-nZVI has a large specific surface area and rich surface charge, and the negative charge on its surface interacts with the charge on the surface of the microplastic, fixing the microplastic on the soil surface through electrostatic adsorption and physical entanglement. In addition, PAL-nZVI can also promote the formation of soil aggregates, make the soil structure more compact, and reduce the migration channel of microplastics in the soil.

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Stabilizing effect of heavy metals

The stabilization effect of PAL-nZVI on Cd and Pb in soil was significant with the prolongation of repair time. The fractions of Cd and Pb in soil were analyzed by BCR continuous extraction method. The results showed that compared with the control group (CK), after 28 days of incubation, the content of weak acid extraction and oxidizable fraction of Cd in soil decreased by 11.55% and 6.48%, respectively, and the content of reducible fraction and residual fraction increased by 6.57% and 11.46%, respectively. The oxidizable Pb content in soil decreased by 22.34%, while the residual Pb content increased by 27.35% (*Figure 5*).

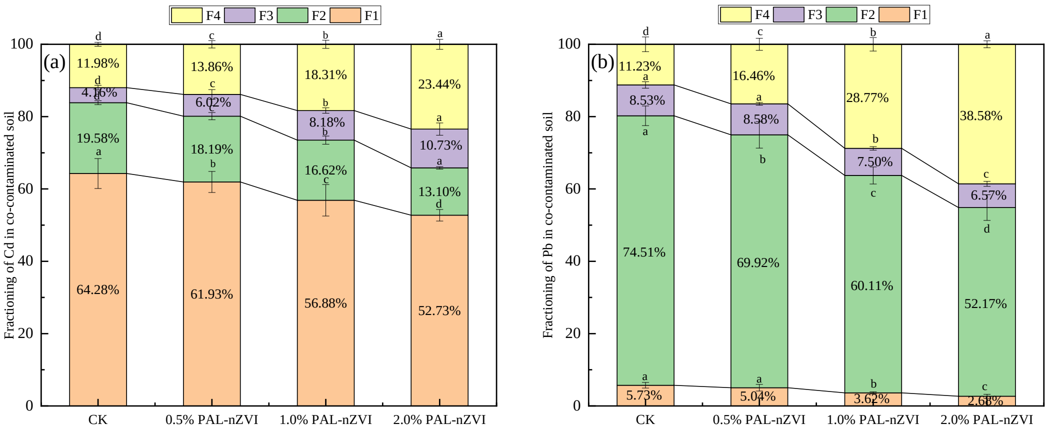

***Figure 5.** Impact of various treatment groups on the fractions of Cd(a) and Pb(b) in soil*

The potential risks of heavy metals are mainly affected by their fraction distribution in the soil, and the toxicity differences between different heavy metals are substantial. According to the potential ecological risk index shown in *Table 1*, it can be seen that when the PAL-nZVI addition amount is 2%, the potential ecological risk (RI) of Cd and Pb decreased by 55.53% and 79.86% compared with CK, respectively. After the BCR continuous extraction method was used to determine the distribution of heavy metals in soil, the residue state (F4) showed good stability, was not easy to migrate in the environment, and had low bioavailability (Nemati et al., 2011). The smaller the SQ, the better the stability of the heavy metals in the soil, and the heavy metals are changing toward a direction that is difficult to migrate, has low biological effectiveness, and has low ecological toxicity. With the addition of PAL-nZVI of 2%, the SQ of Cd and Pb in the soil decreased by 55.45% and 79.87% compared with CK, respectively. With the increase in PAL-nZVI dosing, the heavy metal stabilization rate (RR) has significantly improved. When the PAL-nZVI addition amount was 2%, the RR of Cd and Pb in the soil increased by 11.46% and 27.35% compared with CK, respectively.

The stabilizing effect of PAL-nZVI on heavy metals is mainly achieved by the following mechanisms: first, the strong reducibility of nano zero-valent iron reduces high-valence states of heavy metal ions into low-valance states, reducing their solubility and liability. For example, under acidic conditions nano zero-valent iron reduces Pb^{4+} to Pb^{2+} with the reaction equation: $Fe^0 + Pb^{4+} \rightarrow Fe^{2+} + Pb^{2+}$. Secondly, the adsorption of PAL plays an important role. There are many active sites, such as the silanol group and aluminol group, on the surface of PAL, which can adsorb heavy metal ions through ion

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exchange and surface complexation. In addition, functional groups such as -OH and -COOH on the surface of PAL-nZVI react with heavy metal ions to form stable complexes, further reducing the bioavailability of heavy metals.

Table 1. *Impact of various treatment groups on the RR, RI, and SQ of Cd and Pb in soil*

Treatments	**Cd**			**Pb**		
	RR (%)	**RI**	**SQ**	**RR (%)**	**RI**	**SQ**
CK	11.98±1.15d	220.32±11.63a	7.34±1.04a	11.23±1.21d	39.52±2.15a	7.90±0.87a
0.5%PAL-nZVI	13.86±2.05c	186.44±8.94b	6.21±0.59b	16.46±1.62c	25.38±2.63b	5.08±0.53b
1.0%PAL-nZVI	18.31±1.32b	133.82±13.32c	4.46±0.36c	28.77±2.53b	12.38±1.55c	2.48±0.26c
2.0%PAL-nZVI	23.44±2.53a	97.97±9.55d	3.27±0.64d	38.58±2.11a	7.96 ±0.97d	1.59±0.31d

Note: Different lowercase letters in the same column indicate significant differences between different treatments ($P<0.05$)

Correlation analysis

To further explore the internal relationship between the factors, the correlation analysis of soil physical and chemical properties, enzyme activities, heavy metal stabilization, and microplastic migration was carried out (*Figure 6*). The correlation between soil physical and chemical properties and heavy metal stabilization was found through Pearson correlation analysis that soil pH value was significantly negatively correlated with the reducible fraction (F1) content of Cd and Pb, and significantly positively correlated with the residue fraction (F4) content. This shows that as the soil pH increases, the F1 content of Cd and Pb decreases, and the F4 content increases, which illustrates that the increase in soil pH is conducive to stabilizing heavy metals. The soil cation exchange capacity (CEC) is also significantly negatively correlated with the F1 content of Cd and Pb, indicating that the increase of CEC can effectively reduce the F1 content of heavy metals and enhance its stability. For soil physical and chemical properties and microplastic migration, soil porosity is significantly positively correlated with the microplastic content in deep soil (10-15 cm), which means that the greater the porosity, the easier the microplastics migrate to deep soil. Soil enzyme activity also has a certain correlation with various factors. The microplastic content of surface soil (0-5 cm) can effectively stimulate soil urease and acid phosphatase activities.

Discussion on repair mechanism

According to the experimental results, the mechanism of PAL-nZVI repairing the soil contaminated by microplastic-heavy metals results from multiple synergies. Physical adsorption is the basis of PAL-nZVI interaction with pollutants. The high specific surface area and porous structure of PAL-nZVI enable it to provide many adsorption sites to adsorb microplastics and heavy metal ions through van der Waals forces, electrostatic attraction (Fajardo et al., 2019). For microplastics, the nanoparticles and fiber structures on the surface of PAL-nZVI can be intertwined with the surface of microplastics, increasing the contact area and adsorption force between the two (Song et al., 2023). Chemical reduction is one of the key mechanisms of PAL-nZVI remediation of heavy metal pollution. As a potent reducing agent, zero-valent iron nanoparticles can reduce the high state of heavy metal ions to a low state and reduce their toxicity. As mentioned, zero-valent iron nanoparticles can reduce them to a more stable low-valence state (Xue et al.,

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2018). At the same time, in the reduction process, the nano zero-valent iron itself is oxidized to iron ions, which can be further hydrolyzed to form a precipitate such as iron hydroxide, resulting in co-precipitation of heavy metal ions, thereby fixing heavy metals in the soil (Huang et al., 2018).

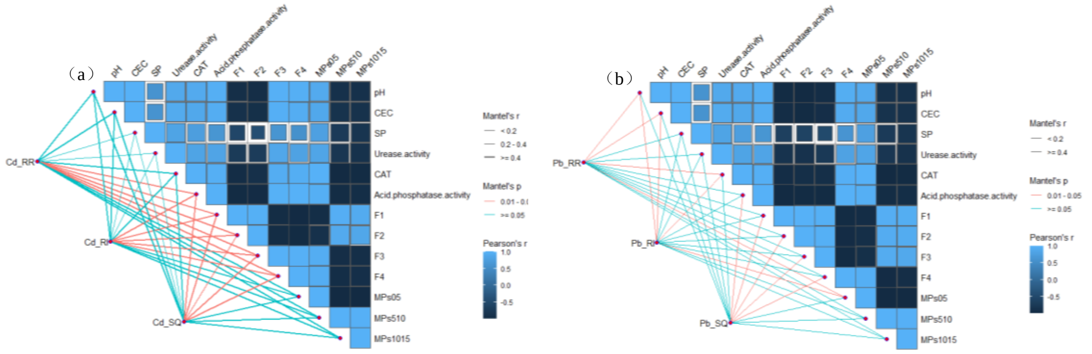

Figure 6. *The correlation analysis of soil physical and chemical properties, enzyme activities, heavy metal stabilization, and microplastic migration. Note: F1, F2, F3 and F4 in Figure 6(a) represent the exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction contents of Cd; F1, F2, F3 and F4 in Figure 6(b) represent the exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction contents of Pb; MPs05 represent the content of microplastics at 0-5 cm depth; MPs0510 represent the content of microplastics at 5-10 cm depth; MPs1015 represent the content of microplastics at 10-15 cm depth*

Surface complexation also plays a vital role in PAL-nZVI remediation of composite contaminated soil. The functional groups on the surface of PAL-nZVI, such as the carboxyl group and hydroxyl group, can react with heavy metal ions to form stable complexes (Zhang et al., 2025). The formation of these complexes not only reduces the activity of heavy metal ions but also changes their migration and transformation behavior in soil. For example, the -COOH functional group can react with Cd^{2+} to form a stable Cd - COO complex (Zhang et al., 2024).

The ion exchange is mainly due to the ion exchange properties of PAL. There are exchangeable cations, such as Na^{+}, Ca^{2+}, etc., in the crystal structure of PAL (Liu et al., 2020). When the heavy metal ions in the soil come into contact with PAL, exchange cations and heavy metal ions can exchange reactions, and the heavy metal ions are fixed on the surface of palgorskite (Wang and Wang, 2016). This ion exchange can effectively reduce the concentration of heavy metal ions in soil solution and reduce its harm to the soil ecosystem.

Conclusion

The PAL-nZVI composite was successfully prepared in this study, and its well-remediation effect on microplastic-heavy metal composite contaminated soil was verified. PAL-nZVI can effectively reduce the migration of microplastics in soil while significantly improving the stability of heavy metals and reducing their bioavailability. The repair mechanism mainly includes physical adsorption, chemical reduction, surface complexation, and ion exchange. This study provides a new technical approach for the remediation of soil contaminated by microplastics and heavy metals and has potential

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application prospects. However, factors such as large-scale preparation, cost-effectiveness, and long-term environmental impact of remediation materials need to be considered in the actual soil remediation process. Future studies can further optimize the remediation process and promote the practical application of this technology.

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