



Fixation Effect of Fe₃O₄-GO to Hinder Pb(II) Translocation into Leek

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Abstract Agricultural soil is easily polluted by heavy metal and recently by metal-based nanoparticles, which has been synthesized in lab and discarded to environment. The uptake and accumulation of them by crops in polluted soil may pose high risks for human health. Here, we investigated the fate and the fixation effect of Fe₃O₄-GO nanocomposites (NCs) to lead ions in the soil-leek system during four harvest lifecycle. The results showed within 100 days, 600-mg/kg Fe₃O₄-GO significantly decreased Pb(II) concentrations in leaves by 37.89%, 39.10%, 73.86%, and 47.17% compared with controls. When Fe₃O₄-GO was added into Pb(II)-polluted soil, a significant fixation effect of Pb(II) was found, and the reduce percentages were 47.29%, 66.60%, 78.04%, and 39.16% for leaves, stem, storage

roots, and absorbing roots compared with controls. The scanning electron microscope images showed that the overall appearance of Fe₃O₄-GO has not been destroyed during the interaction with soil.

Keywords Magnetic graphene oxide · Leek · Pb(II) · Fixation

1 Introduction

Among the environmental pollutants, heavy metal elements, such as Cd(II), Hg(II), Pb(II), Cr(VI), and Cu(II), have accumulation and concealment (Gu et al. 2018).

Highlights • The fate and the fixation effect of Fe₃O₄-GO nanocomposites to Pb(II) in the soil-leek system during four harvest lifecycle were investigated.

- After addition of Fe₃O₄-GO into Pb(II)-polluted soil, a significant fixation effect of Pb(II) was found based on the analysis of leaves, stem, storage roots, and absorbing roots.
- The scanning electron microscope images showed that the overall appearance of Fe₃O₄-GO has not been destroyed during the interaction with soil.

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These heavy metal elements would not only destroy the atmosphere, water, and soil ecological environment but also bring about serious problems in food safety through the enrichment of animals and plants, which would directly endanger human health (Liu et al. 2013).

According to reports, there have been too many heavy metal pollution incidents in the world, which have brought indelible harm (Inaba et al. 2005). Soil heavy metal pollution has become one of the urgent problems in China. In recent years, although China's economy has continued to develop, the area of agricultural land pollution has gradually expanded (Huang et al. 2007). The situation of heavy metal pollution in China's agricultural arable land is not optimistic. According to a preliminary report, the area of arable land polluted by heavy metals such as Pb(II), Cd(II), and As(V) accounted for about 20% of the country's arable land (Bai et al. 2015). In the past 5 decades, about 800,000 t of Pb(II) has been released to the environment worldwide and most of them have been deposited in the soil, becoming a potential high risk (Yang et al. 2018). Heavy metals, deposited in farmland soil, could be accumulated into fruits and vegetables, especially the edible parts of leafy vegetables.

Many small-molecule compounds coupled with nanomaterials, such as Fe₃O₄, could absorb heavy metals and have been studied widely (Ghasemi et al. 2017; Sun et al. 2018). Among of them, Fe₃O₄-GO nanocomposites have unique physical and chemical properties, which make them widely used in the electronics industry, medical sciences, and chemistry (Liang et al. 2010). Numerous researches have reported that Fe₃O₄ or its functional materials could be used in *in vivo* imaging, targeted therapy, and heavy metal removal (Dan et al. 2015; Deng et al. 2008). There is a review which has summarized the characterization and mechanisms for the uptake of engineered nanoparticles by different plant (Rico et al. 2011a). However, Fe₃O₄-GO nanocomposites absorbing heavy metal in soil and fixing effect to reduce metal translocation into plant have been little reported. Zhu et al. have found no absorbing ability of Fe₃O₄ NPs in the soil-plant system and translocation in the plants grown due to their attachment with sand or soil grains (Zhu et al. 2008). However, a large number of nanomaterials can easily enter the water and soil system in the process of production, recycling, and processing, causing potential harm to agricultural cultivation. Therefore, it is urgent to evaluate their impact on the soil. CuO and Fe₃O₄ are two

common metal oxides, and they can cause the bacterial community to be greatly affected by nanoparticles within few days (Simonin and Richaume 2015). Among them, CuO nanoparticle pollution can cause a greater impact, while Fe₃O₄ is less toxic to soil bacterial communities. At the same time, these two materials did not change the total amount of organic matter in the soil and had little effect on the macroscopic properties of the soil (Peng et al. 2017; Anderson et al. 2017). Multi-walled carbon nanotubes and silver nanoparticles could affect the germination rate, chlorophyll, and water-soluble protein content of rice seedlings (Park and Ahn 2016). TiO₂ nanoparticles improved the growth of rice in phosphorus-deficient soils. The addition of TiO₂ NPs increased the phosphorus content in rice roots, stem, and cereals, and the amino acid, palmitic acid, and glycerol content in cereals produced by plants (Zahra et al. 2017). TiO₂ also increased spinach growth and biomass, improved photosynthesis of sage mustard, and inhibited the growth of broad bean roots (Sun et al. 2018; Zhao et al. 2019; Mu et al. 2015). Crops, particularly vegetables, could assimilate heavy metal from farmland and enriched elevated concentrations caused by human activities, such as wastewater irrigation. The above researches mainly studied the toxicity of the addition of nanomaterials to soil and plant growth; the impact of Fe₃O₄-based NPs in the soil and their effect on heavy metal migration in soil and plants are ignored.

Fe₃O₄-GO, as a new type of carbon nanomaterial derived from graphene, is widely used in the removal of heavy metals and organic fields due to its rich oxygen-containing functional groups, large specific surface area, and easy separation (Xiao et al. 2017). Leek is an edible vegetable found throughout Asia, North America, North Africa, and Europe, which has advantages of strong adaptability to the environment, relatively low requirements for cultivation conditions, short growth cycles, continuous harvesting, and heavy metal enrichment (Gonzalez et al. 2003). It has been used as a model plant for study of heavy metal migration from soil-plant system (S-w et al. 2007).

In this paper, pot-culture experiment was used to study the effect of Fe₃O₄-GO in the soil on the migration of Pb(II). Characterization of synthesized Fe₃O₄-GO was finished through scanning electron microscope (SEM), transmission electron microscope (TEM), and Fourier transform infrared spectrometer (FTIR). Interaction of Fe₃O₄-GO with Pb(II) in soil was revealed by the analysis of Pb(II) and Fe(III) concentration change

in the content of Pb(II) and Fe(III) in the leaves, stem, and roots of leek and subcellular fraction of leaves. This is, to the best of our knowledge, the first report on effects of Fe₃O₄-GO application on hindrance Pb(II) translocation into leek over an extended contact period (100 days) under soil conditions.

2 Materials and Methods

2.1 Soil Source and Characteristic

Organic farm soil was obtained from Nanjing. The soil was sieved through mesh sizes of 20, air-dried at room temperature, and stored at 4 °C before use. Sieved soil was also test for their heavy metal concentration and pH.

2.2 Synthesis of Fe₃O₄-GO and Characterization

GO was prepared by using the Hummers method (Chen et al. 2013). In this experiment, Fe₃O₄-GO was synthesized by using the co-precipitation method, which has been reported before (Sun et al. 2018). The characterization referred to the previous report (Sun et al. 2018). TEM and SEM were used to observe the surface morphological characteristics. FTIR was used to analyze the chemical groups, and the scanning range was 4000–400 cm⁻¹.

2.3 Spiking of Soil with Fe₃O₄-GO and Lead

Fe₃O₄-GO was mixed as a powder into soil mechanically 20 min with a mixer. Four pots, named A, B, C, and D, were added with soil containing 0-, 600-, 0-, and 600-mg/kg (dry mass/air-dried soil mass basis) Fe₃O₄-GO separately. Commonly, 1500 g of soil was placed in each plastic flower pot. After 24 h, 500-mg/kg lead (dry mass/air-dried soil mass basis) dissolved in 1-L water was added into pots C and D for 20 days to simulate long-term pollution. The soil/nanoparticle mixtures were stored at 4 °C before planting.

2.4 Leek Cultivation in Soil with Fe₃O₄-GO and Lead

The leek was first cultivated and grown in natural soil. Then, the upper part of leek was cut off, leaving a 5-cm stem on the ground. Then, the leek was uprooted and washed with tap water. The root part was reserved 3–4 cm to promote the development of new roots. The leek

was then transferred to pots A, B, C, and D. In each pot, 15 leeks were planted. The leek is watered every 2 days and harvested every 25 days. There are harvests four times for all the experiments. Finally, Fe₃O₄-GO added in the soil is separated by magnet separation and characterized by TEM, SEM, and FTIR.

2.5 Pb(II) Concentration in Subcellular Components of Leaves and Organ of Leek

Leaves, stem, and roots were collected and digested with HNO₃-H₂O₂. The digestion process followed the method of GB 5009.268-2016, and the concentration of Pb(II) and Fe(III) were determined by ICP-MS.

Subcellular components of leaves were also separated and determined (Allfrey 1959). A 4 °C pre-cooled extraction buffer (250-mM sucrose, 1-mM dithiothreitol, and 50-mM pH 7.5 Tris-HCl solution) was added to fresh leaf sample and has undergone rapid milling at 4 °C. The solid-to-liquid ratio was 1:10. The obtained homogenate was rinsed with extraction buffer. The homogenate was centrifuged at 300 r/min for 30 s. The bottom sediment contained the cell wall of the leaves. The upper suspension was further centrifuged at 20000 r/min for 45 min. The obtained precipitate contained the organelle of the leaves, and the upper solution contained soluble substances, including inorganic ions, organic substances in vacuoles, and cytoplasm. The collected three parts were measured by ICP-MS as described before. All the measurements were repeated 3 times.

3 Results and Discussion

3.1 Recycle and Characterization of Fe₃O₄-GO in Soil

Fe₃O₄-GO, which has been mixed in the soil for 100 days, still maintained high magnetic properties and could be separated from the soil. As shown in Fig. 1, the color of Fe₃O₄-GO separated from soil (Fig. 1b) indicated that Fe₃O₄-GO has adsorbed Fe oxides existed in soil. After cleaning with ultra-pure water several times, the color of recycled Fe₃O₄-GO (Fig. 1c) changed to pristine color, but the Fe oxides was still adsorbed with Fe₃O₄-GO.

The synthesized Fe₃O₄-GO (Fig. 1a and Fig. 2b) was a complex of Fe₃O₄ and GO. As shown in Fig. 2a, GO was a smooth and two-dimensional nanomaterial.

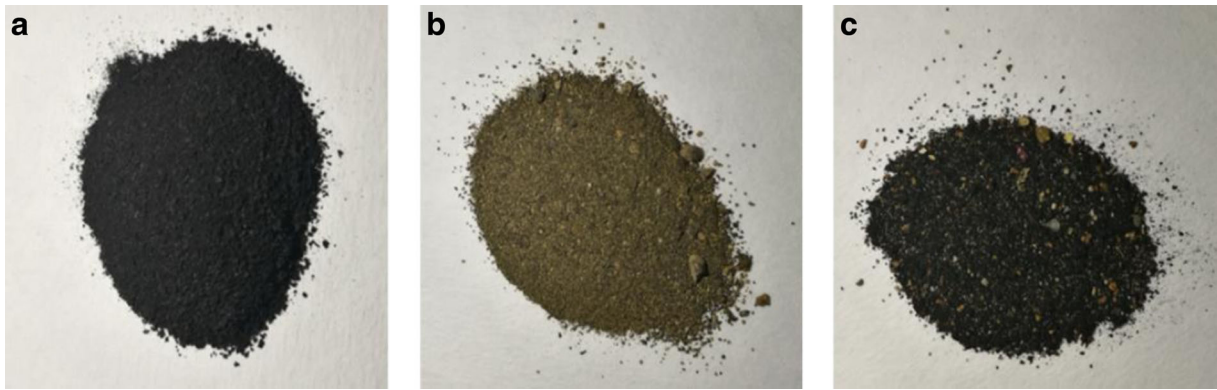


Fig. 1 Macroscopic images of Fe₃O₄-GO (a), recycled Fe₃O₄-GO from soil (b), and recycled and cleaned Fe₃O₄-GO (c)

Multiple wrinkles could be observed on its surface. The magnetic nanomaterial (Fe₃O₄) with a diameter of 15–20 nm was attached to the GO surface in the synthetic process, as shown in Fig. 2b. The morphology of Fe₃O₄-GO was also characterized by SEM in Fig. 2c. The SEM image of Fe₃O₄-GO showed that a large amount of Fe₃O₄ nanoparticles were tightly attached to the surface of the GO sheet. After recycle and wash, the SEM of Fe₃O₄-GO indicated that the morphology and magnetic properties have been maintained (Fig. 2d). However, there were some impurities, which have magnetic

properties and mixed with Fe₃O₄-GO. On the other hand, some studies have found that the addition of nanoparticles had little impact on the macroscopic properties of the soil (Ben-Moshe et al. 2013). This is due to the low nanoparticle addition and low mobility of them.

3.2 FTIR Analysis of Fe₃O₄-GO and GO

As shown in Fig. 3, FTIR spectra of GO, Fe₃O₄-GO, and Fe₃O₄-GO recycled from the soil were obtained. There were some obvious differences among these

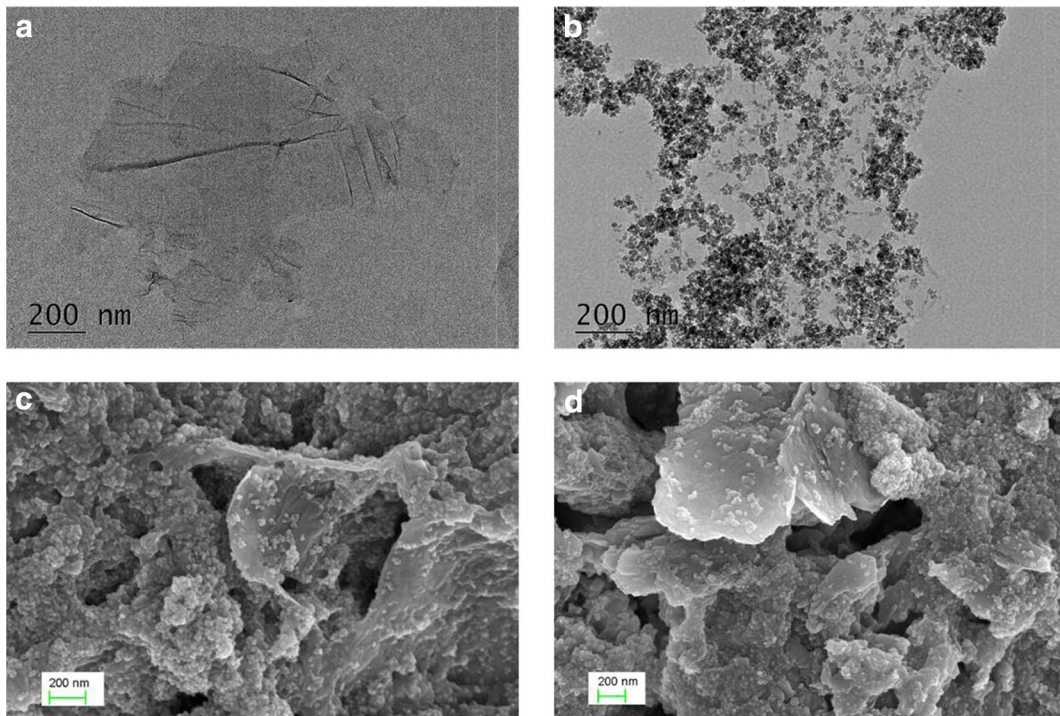


Fig. 2 TEM images of GO (a) and Fe₃O₄-GO (b). SEM pictures of Fe₃O₄-GO (c) and recycled Fe₃O₄-GO from soil (d)

spectra. The strong absorption peak at 3417 cm^{-1} was due to the stretching vibration of -OH , which was blue shifted compared with 3424 cm^{-1} . The stretching vibration of aromatic $\text{C}=\text{C}$ double bond was found at 1631 cm^{-1} . Compared with $\text{Fe}_3\text{O}_4\text{-GO}$ and GO , the symmetric stretching vibration of $\text{O}=\text{C}-\text{O}$ at 1404 cm^{-1} was more obvious. There is a new absorption peak at 1031 cm^{-1} , which is assigned to $\text{Si}-\text{O}$ and $\text{Si}-\text{O}-\text{Si}$ stretching vibrations (Rico et al. 2011b). This peak indicated that muscovite existed in recycled $\text{Fe}_3\text{O}_4\text{-GO}$. Relative to 879 cm^{-1} , a significant red shift occurred at a peak of 893 cm^{-1} . The 893 cm^{-1} and 797 cm^{-1} belonged to the $\text{C}=\text{O}$ stretching vibration or $\text{C}-\text{H}$ bending vibration. The peak at 584 cm^{-1} in Fig. 3B and 583 cm^{-1} in Fig. 3C corresponded to the stretching vibration mode of $\text{Fe}-\text{O}$ in Fe_3O_4 , indicating that the recycled $\text{Fe}_3\text{O}_4\text{-GO}$ maintained the original structure.

According to the above results, it could find that the structure of $\text{Fe}_3\text{O}_4\text{-GO}$ nanomaterials recycled from the soil has not been destroyed and some impurities could not be cleaned as they also have magnetic properties. The SEM of $\text{Fe}_3\text{O}_4\text{-GO}$ showed that the microspheres and the sheet structure were not damaged. The FTIR results showed the absorption peak at 583 cm^{-1} of $\text{Fe}-\text{O}$, indicating that $\text{Fe}_3\text{O}_4\text{-GO}$ in the soil still maintains the physical and chemical characteristics of Fe_3O_4 (G-y et al. 2008). Depended on soil conditions, the fate of nanoparticles was different.

3.3 Pb(II) Concentration in Leek Leaves Obtained by Four Harvests

First, we have investigated the Pb(II) concentration of leek grown in natural soil. The concentration of Pb(II) was 21.39 mg/kg . The pH of the soil was 7.27. Figure 4 presented the content of Pb(II) in leek leaves harvested at 25, 50, 75, and 100 days without Pb(II) artificial pollution. The results showed that the soil added with $\text{Fe}_3\text{O}_4\text{-GO}$ will affect the Pb(II) translocation of plant on it. The highest Pb(II) concentration detected in the four harvests was 1.2 mg/kg (fresh weight), and the addition of $\text{Fe}_3\text{O}_4\text{-GO}$ make the Pb(II) concentration less than 0.3 mg/kg . The primary Pb(II) concentration was near 21 mg/kg , most of them could not be enriched by leaves. This indicated that the original Pb(II) in the soil was uneasy to be absorbed by leek (Rieuwerts et al. 2006). Overall, Pb(II) concentration of leaves from pot A was significantly lower than that from pot B. As shown in Fig. 4, Pb(II) concentration in leaves harvest on the 50th day was maximum, which was 1.37 times than that on the 25th day. For leaves obtained from pot B ($\text{Fe}_3\text{O}_4\text{-GO}$ was added), a gradual decline of Pb(II) concentration was observed. In conclusion, $\text{Fe}_3\text{O}_4\text{-GO}$ has a fixation effect on Pb(II) in soil and hindered their transportation. For pots C and D, Pb(II) was added to soil by spraying for 20 days. The Pb(II) concentration in leaves is detected and shown in Fig. 5. Apparently, a sharp decline trend of Pb(II) concentration for leaves could be

Fig. 3 FTIR spectra of GO (A), $\text{Fe}_3\text{O}_4\text{-GO}$ (B), and recycled $\text{Fe}_3\text{O}_4\text{-GO}$ from soil (C)

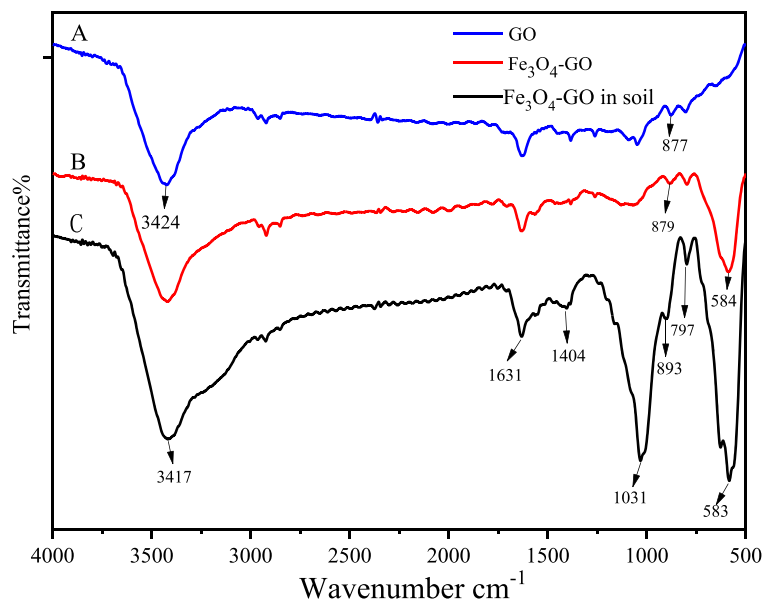
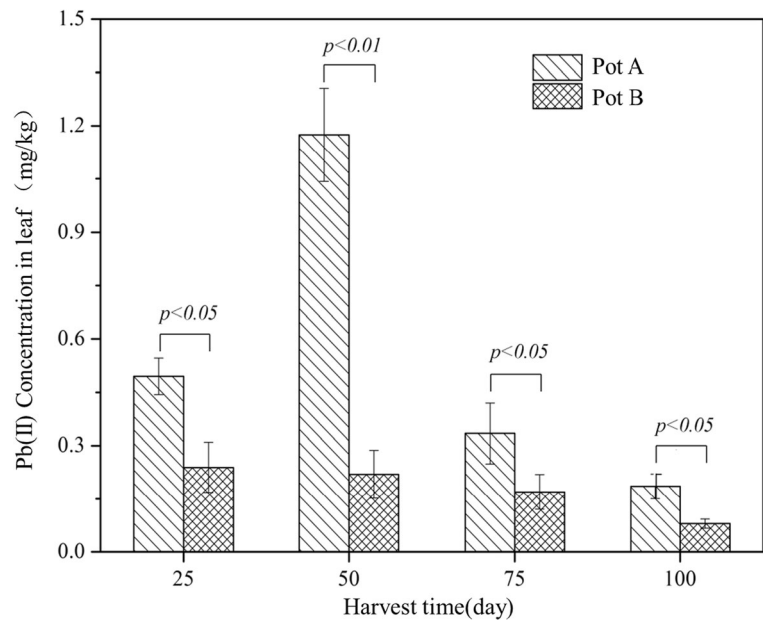


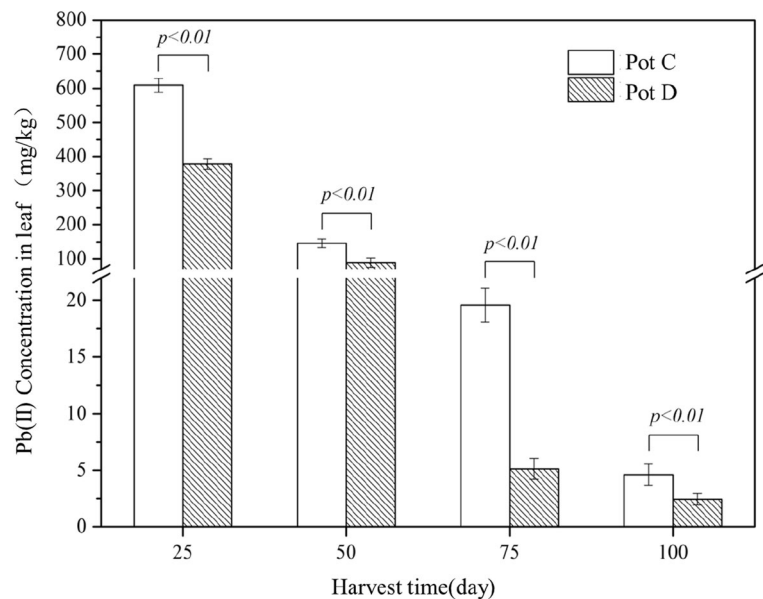
Fig. 4 Pb(II) concentration in leaves harvested at different times without Pb(II) polluted



observed. As free lead ions could be easily enriched by plant, the concentration of Pb(II) in first harvest leaves was around 600 mg/kg. And Fe₃O₄-GO containing soil in pot D could prevent a lot of free lead ions be transferred from roots to leaves. The leaves obtained from pot D showed less than 400-mg/kg Pb(II). The concentration difference between the two samples was extremely significant ($P < 0.01$). Compared with the samples obtained from pots C and D on the 25th, 50th, 75th, and 100th days, Pb(II) concentrations were reduced by

37.89%, 39.10%, 73.86%, and 47.17%, respectively. The results indicated that Fe₃O₄-GO could prevent part of lead ions to be enriched. Pb(II) was bound to the surface of Fe₃O₄-GO by formation of Pb-O bonds. Considering that the soil could also interact with Pb(II) and the proportion of Fe₃O₄-GO in soil was 0.06%, this fixation effect was remarkable as shown in Fig. 5. The application of Fe₃O₄-GO reduced the mobility of Pb(II) in the soil obviously, which was consistent with an earlier report (Chlopecka and Adriano 1997).

Fig. 5 Pb(II) concentration in leaves harvested at different times with Pb(II) polluted



Fe_3O_4 -GO was a nanocomposite containing Fe_3O_4 and GO. The mechanism of metal adsorption on Fe_3O_4 -GO included electrostatic attraction and surface complexation. Electrostatic attraction play an important role for Fe_3O_4 in the adsorption process, and the surface of Fe_3O_4 adsorbents undergoes protonation/deprotonation with pH change. GO has high affinity for many metal ions through surface complexation due to the abundant oxygen-containing functional group on the surfaces of graphene oxide (Sun et al. 2018). Several studies have found that selenium exhibited protective effects against many toxic element heavy metals in the process of plant growth. However, this antagonistic effect was dosage- and speciation-dependent.

Selenium (Se) has been used to counteract the toxicity of cadmium and lead in soil. In soil, Se may influence the formation of iron plaque on rice root surface and then affect Cd uptake (Qingqing et al. 2019). Hu et al. have applied selenium fertilization in soils and found that metal mobility and bioavailability decreased significantly. The translocation factor of Cd and Pb from soil to iron plaque decreased significantly (Hu et al. 2014). Hg-Se complexes could also be formed in soil and reduce the Hg levels in grain, depending on the chemical speciation of Se (Wang et al. 2016).

3.4 Effect of Fe_3O_4 -GO on Pb(II) Distribution in Subcellular Components of Leaves

Pb(II) concentration in the cell wall, organelles, and soluble fractions of leek harvested on the 25th day is

detected and presented in Fig. 6. The Pb(II) concentration in unpolluted leaves was around 100 ng; however, the value was more than 4000 ng for Pb(II)-polluted sample. The Pb(II) distribution followed the order cell wall > organelles > soluble substance. An important result was that Pb(II) concentration of soluble matter was almost very low and only existed in polluted leek, which indicated that the leek was seriously polluted. The Pb(II) distribution in subcellular components of leaves could be regarded as the existence of exogenous pollution stress. The addition of Fe_3O_4 -GO in soil lead Pb(II) concentration decrease 8.15~37.72% in leaves, stem, storage roots, and absorbing roots. The addition of Fe_3O_4 -GO has inhibited the transfer of Pb(II) from soil to roots and no in harm plant. Figure 7 showed the Fe(III) concentration in the cell wall, organelles, and soluble parts. For unpolluted leek, the Fe(III) distribution followed the order organelles > cell wall > soluble matter, which was different from Pb(II) distribution. For polluted leek, the Fe(III) distribution followed the order cell wall > organelles > soluble matter.

Based on the analysis of first harvest leek, Fe(III) was found in three subcellular components of unpolluted leaves, and the addition of Fe_3O_4 -GO reduced the Fe(III) concentration in the cell wall, organelles, and soluble parts by 55.81%, 66.12%, and 24.29%, respectively. The reason might be that Fe_3O_4 -GO absorbed some Fe elements or very high concentration of Pb(II) in the first leek, decreasing the efficiency of Fe(III) transportation. This lead Pb(II) concentration increased, and the Fe(III) concentration reduced in soluble matter.

Fig. 6 Pb(II) amount in subcellular fraction harvested on the 25th day

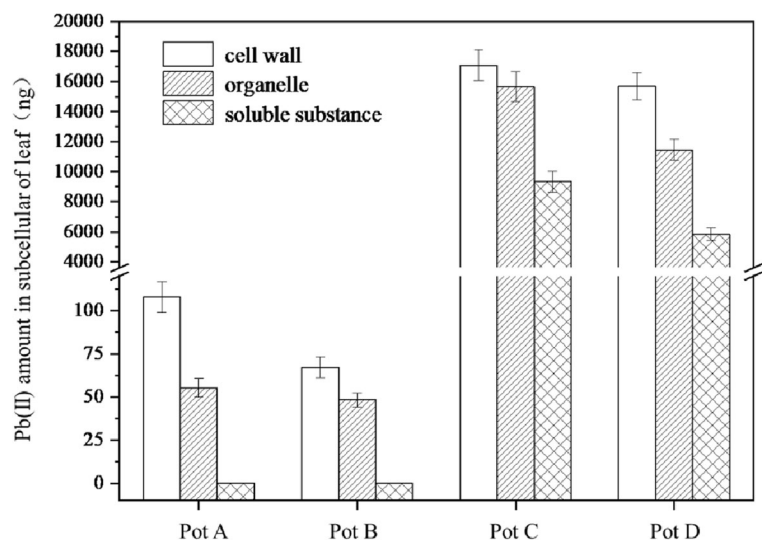
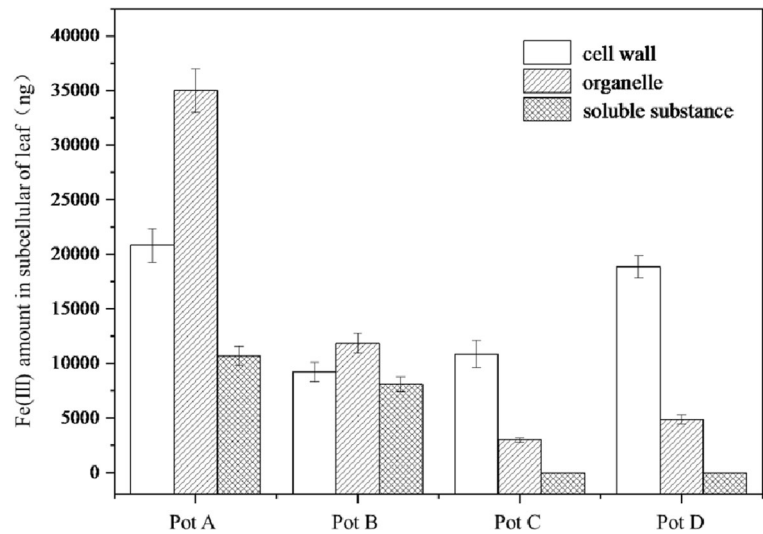


Fig. 7 Fe(III) amount in subcellular fraction harvested on the 25th day



3.5 Effect of Fe₃O₄-GO on Pb(II) Distribution in Leek Organ

Commonly, roots have stronger enrichment effect than leaves. The concentration of Pb(II) in leaves, stem, storage roots, and absorbing roots, which were harvested on 100th day, was shown in Table 1. No matter if Fe₃O₄-GO was added or not, the Pb(II) distribution trend was consistent in the four experiments. The Pb(II) concentration followed the order absorbing roots > storage roots > stem > leaves. As shown in Table 1, Pb(II) concentration in stem and roots obtained from pot D was also obviously lower than that from pot C. This proved again that Fe₃O₄-GO has a significant fixation effect on Pb(II) in the soil under high Pb(II) pollution condition. The reduce percentages were 47.29%, 66.60%, 78.04%, and 39.16% for leaves, stem, storage roots, and absorbing roots. For no Pb(II) pollution leek (pots A and B), the Pb(II) transfer coefficient decreased from 34.91 to

13.24%. For artificial polluted leek, the Pb(II) transfer coefficient decreased from 18.60 to 16.25%. These results revealed that the addition of Fe₃O₄-GO in soil could prevent the migration of Pb(II) from soil to plant. Some other materials, such as rice straw-derived biochar, have been studied before and owned the ability to immobilize Cu(II), Pb(II), and Cd(II) in a simulated polluted Ultisol (Jiang et al. 2012).

On the other side, we have detected Fe(III) concentration in leaves, stem, storage roots, and absorbing roots. As shown in Table S1, slight Fe(III) increase was observed in roots and stem, which was probably caused by the degradation of Fe₃O₄ on GO. However, the Fe(III) concentration increased only in stem and roots, and the transfer coefficient of Fe(III) was lower than 10%. Combined with the SEM results, we can conclude that Fe₃O₄-GO could not enter the soil-plant ecosystem. These results were consistent with a survey, which reveal that Fe₃O₄ could not enter wheat plants.

Table 1 Pb(II) concentration in different organ of leek and transfer coefficient

Experiments	Pb(II) concentration/(mg/kg) (<i>n</i> = 3)				Transfer coefficient % (Leaves + stem)/(storage roots + absorbing roots)
	Leaves	Stem	Storage roots	Absorbing roots	
Pot A	0.18 ± 0.02	0.19 ± 0.02	0.33 ± 0.05	0.73 ± 0.13	34.91 ± 0.04
Pot B	0.08 ± 0.01	0.10 ± 0.02	0.47 ± 0.05	0.89 ± 0.05	13.24 ± 0.01
Pot C	4.61 ± 0.43	9.43 ± 0.47	28.78 ± 1.10	46.22 ± 0.98	18.60 ± 0.78
Pot D	2.43 ± 0.30	3.15 ± 0.12	6.32 ± 0.51	28.12 ± 1.48	16.25 ± 0.01

4 Conclusion

The application of Fe₃O₄-GO reduced Pb(II) mobility in soil and enrichment of Pb(II) in roots, stem, and leaves compared with the control.

The recycled nanoparticles showed that their structure and morphology did not change significantly. The fate and the potential co-transport risks need more new evidence in spite of some reports have shown that nanoparticles could be transported in the soil-to-plant system. After analysis of four harvest leek, results showed that Pb(II) contents in leaves decreased dramatically after the fourth harvest. This revealed that it is reasonable to abandon the first few harvest leek in tradition.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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