Application of fish scale derivatives in ameliorating the phytotoxicity effects of multi-metal contaminated soil on paddy rice

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Abstract

Immobilization is an efficient method in the remediation of heavy metal-polluted soils. A greenhouse experiment is conducted to investigate the influence of fish scale powder, chitin, and chitosan on the growth and chemical composition of rice grown on a soil contaminated with Zn, Pb, Cd, and Ni. Results showed that the application of fish scale powder, chitin, and chitosan significantly increased root and shoot dry matter yield of rice, but decreased Pb phytoextraction efficiency. Further, the translocation factor of Ni decreased following the application of fish scale powder and chitosan. Application of fish scale powder decreased Ni, Cd, Zn, and Pb bioavailability in soil. The addition of chitosan reduced Ni and Pb concentration in rice shoots. Among different amendments, only the application of chitosan had a significant effect on the reduction of Zn content in rice root. Considering that the translocation factors were less than one in all treatments, it can be concluded that biostabilization of the studied metals has occurred. based on the obtained results fish scale derivatives including fish scale powder and chitosan play an important role in the removal of heavy metals due to having suitable functional groups. Therefore, it can be deduced that due to the economic feasibility, environmentally friendly, and high metal removal capability of chitosan and fish scale powder, these two amendments are highly recommendable to be applied in multi-metal polluted soils for increasing metals removal and hence decreasing their phytotoxicity.

Introduction

Hazardous heavy metals (HMs) pollution from anthropogenic sources and natural inputs is a major threat to human health (Kamari et al. 2011; Liphadzi and Kirkham 2006). Accumulation of HMs in agricultural soils is a serious and increasing problem because of rapidly growing industrial areas, and excessive use of chemical fertilizers and sewage wastes (Li et al. 2005; Wong et al. 2002; Zeng et al. 2008; Zhao et al. 2010). Increasing HMs in agricultural soils can result in a decrease in soil fertility, crop yield losses, and the entrance of HMs to the food web through plants, causing serious implications for animal and human health (Cui et al. 2018; Kang et al. 2016; Lahori et al. 2017; Xiong et al. 2016; Zibaei et al. 2020). It has been shown that long-term exposure of human beings to some HMs such as Cd, and Pb increase the risk of mortality from cancer (Fan et al. 2017; Wang et al. 2011). While previously most researchers studied soils polluted with a single HM, recently, more attention has been paid to the multi-metal polluted soils (Razmi et al. 2021; Su 2014).

Rice is a significant dietary source that is consumed by more than half of the world's population (Fao 2012; Rabbani et al. 2015). This plant may assimilate a substantial amount of HMs from polluted soil due to its high biomass and exponential growth(Arao et al. 2010; Guo et al. 2020). The consumption of rice contaminated with HMs can lead not only to mental health disorders but to many debilitating diseases(Guo et al. 2020). Hence, the accumulation and transference of HMs into a soil–rice system have become a mounting concern (Zhao et al. 2010).

The mobility and bioavailability of heavy and trace metals in the environment are affected by adsorption and desorption in soils (Martinez-Villegas et al. 2004; Mayel et al. 2014). Diverse soil properties such as pH, organic matter content, cation exchange capacity (CEC), oxidation-reduction status (Eh), the contents of clay minerals, and calcium carbonate are closely related to the adsorption-desorption process (Antoniadis et al. 2008; Kashem and Singh 2001; Zeng et al. 2011). It appears that among different soil properties, soil pH plays the most important role in controlling HMs bioavailability (Zeng et al. 2008). The mobility and bioavailability of most HMs increase with decreasing soil pH (Badawy et al. 2002; Du Laing et al. 2009; Wang et al. 2006). Flooding of paddy soils causes changes in the values of soil pH, as well as redox potential and makes the paddy field a complex system. Such changes in soil properties may influence the negative charges of soil that are important in the adsorption of metals and hence their solubility (Hussain et al. 2021; Li et al. 2014). The content of CaCO_3 considerably impacted the activities of HMs in soil and their absorption by the plant (Wang et al. 2020; XIAN et al. 1988).

When HMs contamination of soil exceeds a certain threshold, soil loses its natural capacity to control the availability of metal ions consequently soil degradation occurs. Therefore, soil remediation technologies are required under such circumstances (Raicevic et al. 2005; Shi et al. 2009; Sunarso and Ismadji 2009). Various soil remediation techniques have been employed to reduce the risks associated with HMs efflux into soil, including soil removal and replacement, soil washing, phytoremediation, and in-situ immobilization (Bolan et al. 2014; Yin et al. 2015). From the view of being fast and economical, in situ immobilization is a well-known method. This method reduces the availability of metal ions through sorption, complexation, and precipitation using organic/inorganic amendments (Chauhan et al. 2012; Tripathi et al. 2018; Yin et al. 2015).

One of the fundamental aspects of the fishing industry in Iran is the presence of different seas and rivers in different parts of this country (Ghobadian 2012). The by-products of fish processing are considerable quantities that usually include unwanted parts such as shellfish, unused and underused items (Wasswa et al. 2007). Immense quantities of waste materials that remain in the environment create pollution and health problems. Hence, the recovery of value-added products from these residues constitutes an important waste reduction strategy (Kongsri et al. 2013; Pal and Maiti 2020). Among the polysaccharide in the marine environment, chitin (CTN) has attracted much attention as the second most available natural polymer after cellulose (Muxika et al. 2017; Silva et al. 2012). It can be converted into chitosan (CTS) through deacetylation (Ghasemi-Fasaei et al. 2021; Muxika et al. 2017). Functional groups are particularly effective in immobilizing metals due to their ability to bind or complex them. The presence of numerous amino and hydroxyl groups in CTS illustrates a high adsorption potential for HMs (Chu 2002; Dhakal et al. 2005; Tripathi et al. 2017). The molecule of CTS consists of amino and hydroxyl groups that can act as binding sites for metal ion complexation. It is a powerful chelating agent and possesses high adsorption capacity for a variety of HMs including Zn, Cu, and Hg. In addition, the absence of poisoning effects along with its fast decomposition makes CTS appropriate to be used in various environments (Uthairatanakij et al. 2007).

This study aims to investigate the impact of fish scales powder (FSP), CTN, and CTS on the amelioration of HMs phytotoxicity in rice grown on a soil contaminated with Zn, Ni, Cd, and Pb. To the best of our knowledge, this is the first study of the impact of fish scales and its derivatives on multi-metal contaminated soil on paddy rice.

Materials And Methods

Soil collection and analysis

Sufficient soil samples to prepare a composite sample were collected from the surface horizon (0–30 cm) of Bajgah Agricultural Experiment Station, Shiraz University, Shiraz, Iran, in the southern Iran (29° 35' N, 52°35' E). Some properties of the composite sample were determined using standard methods. The amounts of sand, silt, and clay were 30, 34, and 36%, respectively. The values of electrical conductivity (EC) and cation exchange capacity (CEC) were 0.13 dS m⁻¹, and 26 cmol₍₊₎ kg⁻¹, respectively. The pH value in saturated paste was 7.7.

Preparation of amendments

Mahisefid, *Rutilus frisii kutum*, is a cyprinid fish which is an important economic species in the Caspian Sea (Abdolhay et al. 2010). The fish scales of mahisefid (Caspian kutum) collected from local markets in Anzali port, Gilan province, Iran. Fish scales were separated from fish waste, washed with distilled water and sun-dried for two days. The sun-dried materials were oven dried and powdered to make FSP to be used as an amendment and as raw material for the preparation of other amendments of CTN and CTS (Ghasemi-Fasaei et al. 2021).

Treatments and experimental design

Soil samples were contaminated with 125 mg.kg⁻¹ of each Cd, Zn, Pb, and Ni as nitrate sources and incubated for one month at 25 ± 2°C under saturated moisture. The experiment was carried out in a completely randomized design with 4 amendments (control, 0.5% FSP, 0.5% CTN, and 0.5% CTS). After incubation, the contaminated soils were transferred to 2 kg pots and six rice seeds were sown in each pot and thinned to three uniform stands one week after emergence.

Plant harvest and tissue analyses

The rice was harvested after 7 weeks of growth, and then shoots and roots were separated from soil. Both parts were washed carefully, oven-dried, weighted, and powdered. Following the method described by (Yingang et al. 2018), each sample (one gram of plant material) was digested in a mixture of hydrochloric acid and nitric acid with a ratio of (1: 3) at 180°C for one hour. Then, two mL of 30% H₂O₂ were added. This procedure was repeated one more time to make sure that the digestion process was completed. The sample was next diluted to the final volume of 50 mL with nitric acid. The concentrations of Zn, Pb, Ni, and Cd were determined using an atomic absorption spectrophotometer (Shimadzu AA 670 G, Japan).

Calculations and statistical analyses

The values of phytoremediation criteria were calculated using the following equations.

Translocation factor (TF) = metal content in aerial part /metal content in root

Phytoextraction efficiency (PE) ($\mu\text{g g}^{-1}$) = shoot metal uptake/ root dry weight

Uptake efficiency (UE) ($\mu\text{g g}^{-1}$) = (shoot metal uptake + root metal uptake)/ root dry weight

Data were statistically analyzed using analysis of variance of a one-way factor of a completely randomized design, and means were compared by the Duncan's Multiple Range Test at 5% level of significance using SAS software packages (Ver 9.3).

Results And Discussions

Root and shoot dry matter yield

According to the results, the addition of amendments significantly increased the mean root and shoot dry weight of rice as compared to the control (Figure 1). Application of FSP, CTN, and CTS increased shoot dry weight of rice by 255,105, and 86.6%, and root dry weight of rice by 112, 124, and 72.7%, respectively, as compared to the control. The highest shoot dry weight was observed following the application of FSP to the multi-metal polluted soil (Figure 1). Results of a previous research indicated that FSP treatment considerably improved all morphological characters of *Vigna radiata L.* in a calcareous soil, probably due to the role of FSP as an organic fertilizer that improves soil properties(Alkhafaji and Elkheralla 2019).

Previous studies have reported that the application of CTS had positive effects on the dry biomass of sunflower (Turan et al. 2018b), lettuce(Turan 2019), and calendula (Heidari et al. 2020). It appears that CTS improves plant growth through the enhancement of the uptake of essential elements that is resulted from its ability to chelate ions (Chatelain et al. 2014; Heidari et al. 2020; Katiyar et al. 2015). In addition, the presence of about 7.8% nitrogen in CTS, which acts as a nitrogen source for plants can also lead to an increase in plant biomass (Kamari et al. 2011).

The concentrations of Pb in rice shoot and root are illustrated in Figure 2. According to this figure, FSP was the most effective treatment in reducing Pb concentrations in rice shoot. The presence of amino, carboxylic, phosphate and carbonyl groups in FSP can lead to the sorption of Pb (Nadeem et al. 2008). (Gilmour et al. 2013), and (Zhang et al. 2010) reported that the utilization of FSP leads to the immobilization of HMs in polluted sediment. The possible reason behind this phenomenon can be that the precipitation of Pb hydroxides resulted from the connection of Pb^{2+} ions with FSP via ionic bonds (Pal and Maiti 2020).

Compared to control, the application of CTS and FSP treatments caused 50, and 65% decrease in shoots Pb concentration, respectively. Also, the application of FSP, CTN, and CTS caused significant decreases in mean root Pb concentration as compared to control treatment. Positive effects of CTS in decreasing metals uptake by rapeseed has been reported by (Kamari et al. 2012). The addition of CTS as a natural polymer compound that is not degraded easily in alkaline soil leads to an increase in the content of OM and reduced the impacts of Pb during a two-year experimental period (CHANG et al. 2020). In addition, the presence of organic-Ca, amino, and hydroxyl functional groups in CTS can form stable chelates with Pb, and hence alleviate the harmful effects of Pb in the soil through decreasing in the contents of bioavailable Pb in soil (Koptsik 2014; Zhang et al. 2011).

According to the data given in figure 3, the application of FSP and CTS significantly decreased the contents of Ni in rice shoots as compared to control. The lowest contents of Ni in rice shoots are found in plants of FSP treatment. It is likely that the adsorption of HM ions such as Ni^{2+} by FSP showed that ion exchange reaction can decrease metal solubility (Shaikhiev et al. 2020; Villanueva-Espinosa et al. 2001). Application of CTS noticeably reduced Ni concentration in rice root. The results of the present study are in agreement with the results obtained from an earlier study (Heidari et al. 2020) which showed that calcareous soil amended with CTS reduced Ni concentration in plants shoots. Also, it has been reported the use of CTS reduced Ni bioavailability in lettuce through the immobilization of Ni in contaminated soils (Turan 2019). (Turan et al. 2018a) also reported that CTS significantly decreased the concentrations of Ni in the brinjal plant. Results indicated that the use of FSP had a significant effect on the metals immobilization due to the involvement of the carbonyl, nitro and amino groups in FSP (Othman et al. 2016). Although CTN has unique properties such as biocompatibility, bioactivity, and biodegradability, its poor solubility is the main factor limiting CTN utility (Muxika et al. 2017). The lower efficiency of CTN in the adsorption of some metal ions can be attributed to its lower functional groups compared to CTS (Camci-Unal and Pohl 2010).

None of the studied amendments had a significant effect on Cd concentration of rice shoot (Figure 4). The absorption of some HMs such as Cd from soil solution by rice is extensively affected by the redox potential of the soil (Watanabe et al. 1996; Zazoli et al. 2006). During flooding, Cd may be immobilized and precipitates as CdS , while under aerobic conditions, CdS is dissolved and released as Cd^{2+} (Huang et al. 2013; Sun et al. 2007). Addition of FSP significantly decreased Cd content of rice root in comparison with the control. Although CTN, and CTS reduced the Cd concentration in rice roots, these decreases were not statistically significant. (Pal and Maiti 2020) observed that the use of FSP immobilized HMs in contaminated sediment. It appears that the presence of amide, carbonate, and phosphate functional groups were responsible for Cd and Pb ions sorption on FSP biosorbent surface. The polymeric arrangement of FSP biomass is responsible for the presence of negative charges that are derived from the ionization of organic and inorganic functional groups on its surface (Nadeem et al. 2008).

Application of CTS caused a significant decrease in the content of Zn in the root of plants as compared to the control. However, the use of FSP and CTN had no significant impact on Zn concentration compared to the control (Figure 5). It's likely that organic matter forms a coordination complex with Zn based on

Lewis's acid-base theory. Hence, this can be acceptable that Zn^{2+} ions act as the acid and electron pair acceptors which react with CTS that acts as a base (Gerente et al. 2007). The cause of Zn reduction in plant tissues following CTS application can be attributed to Zn immobilization (Park et al. 2011).

Phytoremediation criteria

The values of uptake efficiency (UE), phytoextraction efficiency (PE), and translocation factor (TF) are given in Table 1. Results showed that the application of FSP increased the values of UE for Ni and Zn. However, the addition of amendments had no significant effect on the values of UE for Cd, and Pb. The addition of studied amendments significantly decreased PE of Pb in rice plant tissue. Following the application of CTS, the TF values of Ni significantly decreased in comparison with the control treatment. The value of TF is the ratio of metal concentration in root to that of shoot (Asilian et al. 2018) and demonstrates the ability of a plant to transfer metals from the roots to the shoots (Kutrowska et al. 2017). In the case of Ni, the TF value decreased with applying FSP, and CTS treatments, whereas CTN had no significant impact on the transport of Ni from the root to shoot of rice (Table 1). It is likely that the high efficacy of CTS for Ni chelating is owing to the existence of a large number of amino and hydroxyl groups in its structure that led to declining Ni phytoavailability in soil and consequently lowering the uptake of this metal by rice. Consistent with our results, it has been reported that soil amendment with CTS immobilized Ni in soil and reduced Ni content in lettuce (Turan 2019). The addition of FSP decreased the mean TF value of Ni in the rice plant (Table 1). If values of TF is >1 , then plants has a high potential for metal accumulation in the roots and TF value of greater than 1, indicates the plant's ability to transfer metals from root to the shoot that this characteristic plays a significant role in the phytoextraction of HMs from polluted soils (Baker and Brooks 1989; Cunningham et al. 1995). Overall, the fact that the values of TF for all studied metals were lower than one, demonstrated that rice maintains most of the metals in its root tissues and phytostabilization is the main mechanism of this plant in confronting high levels of the studied metals (Asilian et al. 2018; Cunningham et al. 1995)

Table 1
Effect of FSP and its derivatives on the translocation factor, phytoextraction efficiency, and uptake efficiency of metals in rice plant.

treatment	metal	Translocation factor	Phytoextraction efficiency($\mu\text{g g}^{-1}$)	Uptake efficiency ($\mu\text{g g}^{-1}$)
C	Ni	0.44 a	146.35 a	141.21 b
FSP	Ni	0.29 b	131.51 a	173.15 a
CTN	Ni	0.36 ab	94.07 ab	155.31 ab
CTS	Ni	0.29 b	70.02 b	108.63 c
C	Zn	0.32 a	126.58 a	167.94 b
FSP	Zn	0.30 a	199.38 a	283.58 a
CTN	Zn	0.34 a	102.77 a	174.71 b
CTS	Zn	0.54 a	134.01 a	200.74 b
C	Cd	0.37 a	75.04 a	125.87 a
FSP	Cd	0.04 b	18.29 c	117.39 a
CTN	Cd	0.23 a	44.78 b	141.11 a
CTS	Cd	0.41 a	92.24 a	137.27 a
C	Pb	0.44 a	235.84 a	217.27 a
FSP	Pb	0.38 a	140.09 b	160.19 a
CTN	Pb	0.45 a	127.27 b	153.91 a
CTS	Pb	0.47 a	140.82 b	153.94 a
Mean values with the same letters are not significantly different according to Duncan's multiple range test ($p \leq 0.05$). C: control; FSP: fish scale powder; CTN: chitin; CTS: chitosan.				

Conclusion

Application of fish scale powder and chitosan noticeably reduced the values of Pb, and Ni concentration in the root and aerial parts of rice grown on the heavy-metal polluted soils. Chitosan amendment effectively decreased root Zn concentration, probably due to the abundance of reactive functional groups in this biosorbent amendment. Maximum accumulation of metals in rice root tissues suggested the weakness of this plant in translocating metals from root to shoot and the presence of phytostabilization as the main remediation mechanism. Fish scale derivatives play significant roles in the removal of metals by complexing metals ions in contaminated soils. Hence, the utilization of fish scale derivatives especially CTS and FSP not only can reduce substantial amounts of solid wastes but also is an

economical and efficient technique in decreasing HMs phytotoxicity through the bioadsorption of these metals in polluted soils.

Declarations

1. Ethical Approval: Not applicable.

2. Consent to Participate: Not applicable.

3. Consent to Publish: Not applicable.

4. Authors Contributions:

- Sahar Maleki-Roudposhti: Software, Data curation, Investigation, Resources, and Writing- review & editing.
- Reza Ghasemi-Fasaei: Supervision, Project administration, Formal analysis, and Writing - original draft.
- Abdolmajid Ronaghi: Supervision, Project administration.
- Majid Baghernejad: Supervision, Project administration.

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7. Availability of data and materials: All data generated or analysed during this study are included in this published article (and its supplementary information files).

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Figures

Figure 1

Effects of amendments (C:control; FSP:fish scale powder; CTN:chitin; CTS:chitosan) on shoot (a) and root (b) dry weight of rice grown on a polluted soil. In each part, mean values with the same letters are not significantly different according to Duncan's multiple range test ($p \leq 0.05$).

Figure 2

Effects of amendments (C:control; FSP:fish scale powder; CTN:chitin; CTS:chitosan) on Pb concentration in aerial parts (a) and roots(b) of rice grown on a polluted soil. In each part, mean values with the same letters are not significantly different according to Duncan's multiple range test ($p \leq 0.05$).

Figure 3

Effects of amendments (C:control; FSP:fish scale powder; CTN:chitin; CTS:chitosan) on Ni concentration in aerial parts (a) and roots(b) of rice grown on a polluted soil. In each part, mean values with the same

letters are not significantly different according to Duncan’s multiple range test ($p\leq0.05$).

Figure 4
Effects of amendments (C:control; FSP:fish scale powder; CTN:chitin; CTS:chitosan) on Cd concentration in aerial parts (a) and roots(b) of rice grown on a polluted soil. In each part, mean values with the same letters are not significantly different according to Duncan’s multiple range test ($p\leq0.05$).

Figure 5

Effects of amendments (C:control; FSP:fish scale powder; CTN:chitin; CTS:chitosan) on Zn concentration in aerial parts (a) and roots(b) of rice grown on a polluted soil. In each part, mean values with the same letters are not significantly different according to Duncan's multiple range test ($p \leq 0.05$).