Ecotoxicology and Environmental Safety 161 (2018) 409–419

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Promoting the productivity and quality of brinjal aligned with heavy metals immobilization in a wastewater irrigated heavy metal polluted soil with biochar and chitosan

Veysel Turan[a], Shahbaz Ali Khan[b], Mahmood-ur-Rahman[c], Muhammad Iqbal[b], Pia Muhammad Adnan Ramzani[d,*], Maryam Fatima[b]

[a] Institute of Soil Science and Plant Nutrition, Faculty of Agriculture, Bingöl University, 12000 Bingöl, Turkey
[b] Department of Environmental Sciences and Engineering, Government College University, Faisalabad, 38000 Pakistan
[c] Department of Bioinformatics and Biotechnology, Government College University, Faisalabad 38000, Pakistan
[d] Cholistan Institute of Desert Studies, The Islamia University of Bahawalpur, 63100, Pakistan

ARTICLE INFO

Keywords:
Wastewater
In situ immobilization
Antioxidant enzymes
Nutritional quality
Metals

ABSTRACT

Depleting aquifers, lack of planning and low socioeconomic status of Pakistani farmers have led them to use wastewater (WW) for irrigating their crops causing food contamination with heavy metals and ultimately negative effects on human health. This study evaluates the effects of chitosan (CH) and biochar (BC) on growth and nutritional quality of brinjal plant together with in situ immobilization of heavy metals in a soil polluted with heavy metals due to irrigation with wastewater (SPHIW) and further irrigated with the same WW. Both CH and BC were applied at three different rates i.e. low rate [(LR), BC0.5%, CH0.5% and BC0.25% + CH0.25%], medium rate [(MR), BC1%, CH1% and BC0.5% + CH0.5%] and high rate [(HR), BC1.5%, CH1.5% and BC0.75% + CH0.75%]. Result revealed that brinjal growth, antioxidant enzymes, and fruit nutritional quality significantly improved from LR to HR for each amendment, relative to control. However, these results were more prominent with BC alone and BC + CH, compared with CH alone at each rate. Similarly, with few exceptions, significant reduction in Ni, Cd, Co, Cr and Pb concentrations in the root, shoot and fruit were found in sole CH treatment both at LR and MR but in both CH and BC + CH treatments at HR, relative to control. Interestingly, the concentrations of Fe in the roots, shoots and fruit were more pronounced at BC treatments relative to CH and BC + CH treatments at each rate, compared to control. Overall, the BC + CH treatment at HR was the most effective treatment for in situ immobilization of heavy metals in SPHIW and further irrigated with the same WW, compared to rest of the treatments. This study indicates that BC0.75% + CH0.75% treatment can be used to reduce mobility and bioavailability of heavy metals in SPHIW and facilitates plant growth by improving the antioxidant system. However, the feasibility of BC0.75% + CH0.75% treatment should also be tested at the field scale.

1. Introduction

The rapid increase of population in most of developing countries like Western Africa, Southern Africa and South Asia put significant pressure on water resources. In these severe water-stressed regions, there exists a strong competition for scarce water resources among households, industry and agriculture (Alcamo et al., 2017). In Pakistan, the use of substantial volumes of groundwater as an irrigation source for the production of crops and fodder has already depleted the aquifers (Kirby et al., 2017). Likewise, the lack of planning and limited economic resources are also primarily contributing to the contamination of agricultural soils through anthropogenic activities like irrigation of these soils with industrial and municipal wastewater (WW) (Yan et al., 2018). This WW consists of non-biodegradable heavy metals like nickel (Ni), copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), arsenic (As), mercury (Hg) and zinc (Zn) (Fang et al., 2018; Huang et al., 2017) and appreciable amount of beneficial nutrients of agricultural importance (Chandran et al., 2012). Unfortunately, the poor farmers in Pakistan are compelled to use WW for irrigating their crops because of their low economic status (Minhas and Samra, 2004; Zia et al., 2017). Over time, the constant application of WW to the agricultural soils elevates the concentrations of heavy metals in them, and resultantly,

* Correspondence to: Cholistan Institute of Desert Studies, The Islamia University of Bahawalpur, 63100, Pakistan.
E-mail address: dr.piamuhammad@iub.edu.pk (P.M.A. Ramzani).

https://doi.org/10.1016/j.ecoenv.2018.05.082
Received 21 October 2017; Received in revised form 21 May 2018; Accepted 29 May 2018
0147-6513/

threatens human health via their entry in the food chain (Balkhair and Ashraf, 2016; Islam et al., 2017; Ullah et al., 2018).

Brinjal (*Solanum melongena* L.) belongs to Solanaceae family, is considered one of the safest quality vegetables and widely consumed due to its high nutritional value and an appreciable level of antioxidants (Ai et al., 2018). Meanwhile, WW irrigation containing heavy metals adversely influences the length of shoot and root, and fresh/dry biomass (Madan and Saxena, 2012), fruit yields (Balkhair, 2016; Cirelli et al., 2012), oxidative damage (Fikret et al., 2013; Singh and Prasad, 2014), antioxidant defense mechanism (Cansaran-Duman and Aras, 2015), nutritional quality (Cikili et al., 2016; Shilev and Babrikov, 2005) as well as increases the concentrations of toxic metals in the aerial parts of brinjal (Chandran et al., 2012; Roy and Gupta, 2016).

While keeping in view the limitations of conventional remediation approaches used for heavy metals polluted soils (Ayangbenro and Babalola, 2017; Oberai and Khanna, 2018), the in-situ remediation techniques like immobilization of metals in the soil using organic and inorganic amendments is obtaining fervent attention of the researchers during recent years (Karer et al., 2018; Shahbaz et al., 2018a, b). Biochar (BC) is produced using organic feedstock under pyrolysis condition (Khan et al., 2017; Shahbaz et al., 2018a, b) and exhibits exclusive characteristics like porosity, a large surface area and high cation exchange capacity (CEC) (Cheng et al., 2017; Rajapaksha et al., 2016). Therefore, the incorporation of BC into the soil increases soil pH, water holding capacity (WHC) and CEC (Mohan et al., 2018) which, as a result, contributes for the sorption of metals on the large surface areas of BC (Patra et al., 2017). Biochar also improves soil health and fertility through the provision of essential nutrients to plants (Pandit et al., 2018). In metal polluted soils, the incorporation of BC into them positively influences the biomass (Al-Wabel et al., 2015), antioxidant defense machinery and nutritional quality (Khan et al., 2017; Ramzani et al., 2017a, b; Shahbaz et al., 2018a, b) of plants. While in parallel to BC, chitosan (CH) is a bio-waste derived from the de-acetylated product of chitin isolated from the exoskeletons of crustaceans and is a naturally occurring biopolymer (Abdou et al., 2008). Interestingly, the choice of using CH in heavy metals contaminated soils for immobilization of heavy metals in them sounds a promising technique as CH is a powerful chelating agent having high adsorption potential for metals due to a large number of free amino and hydroxyl groups (Chu, 2002; Dhakal et al., 2005: Turan et al., 2017). Researchers have already confirmed the positive role of CH for immobilization of heavy metals in metal polluted soils (Shaheen et al., 2015; Tripathi et al., 2016; Turan et al., 2017) and heavy metals removal from WW (Gerente et al., 2007; Shi et al., 2017). Interestingly, the application of CH in soil reduced metals uptake in plants (Kamari et al., 2011) which, as a result, improved their growth, antioxidant defense machinery and nutritional quality (Hernández-Hernández et al., 2018; Turan et al., 2017; Zong et al., 2017).

Till now, BC has been extensively used to immobilize heavy metals in the soil polluted with heavy metals due to irrigation with wastewater (SPHIW) (Wagner and Kaupenjohann, 2014, 2015). Similarly, numerous studies have also confirmed the positive role of CH for immobilization of heavy metals in the soils receiving effluent from electroplating industry (Turan et al., 2017) and in a grassland at the lower course of the Wupper river (Shaheen et al., 2015). However, the effects of BC and CH (alone and in combinations at various rates) as heavy metals immobilizing agents mixed in SPHWI, further receiving WW and their associated influences on biomass, antioxidants defense machinery and nutritional quality of brinjal (*Solanum melongena* L.) have not yet been investigated. Therefore, the objectives of this study were (i) to test the role of BC and CH (alone and in combinations at various rates) for immobilization of Ni, Cd, Co, Cr, and Pb in an SPHWI and further irrigated with the same WW; (ii) to monitor the beneficial effects of these immobilizing agents on biomass, antioxidant defense machinery and nutritional quality in brinjal and (iii) to select the most potent combination of BC and CH in terms of its efficiency for the amelioration of heavy metals toxicity in brinjal grown on SPHWI and further irrigated with the same WW.

2. Materials and methods

2.1. Collection and characterization of SPHIW and WW

Soil polluted with heavy metals due to irrigation with wastewater (SPHIW) [0–15 cm (top layer)] used in this experiment was collected from an arable field being irrigated with wastewater (WW) since the last fifteen years in Faisalabad, Pakistan. Prior to use in this experiment, the SPHIW was air-dried, cleaned and sieved through 2 mm sieve. A sub-sample of collected SPHIW was used to determine its physicochemical properties. The soil texture was clay loam and was determined by using hydrometer method (Gee and Bauder, 1986). The electrical conductivity (EC) and pH of SPHIW were measured (at 25 °C) in a saturated soil paste by using a calibrated EC meter (BANTE, DDS-12DW, China) and pH meter (model WTW 7110, Weilheim, Germany), respectively, after shaking the soil-water suspension (1:2.5, soil: de-ionized water) for 1 h. The contents of soil organic matter in SPHIW were estimated by the Walkley-Black method proposed by Nelson and Sommers (1982). Similarly, the contents of $CaCO_3$ in the SPHWI were estimated by adopting the procedure proposed by Allison and Moodie (1965). Water holding capacity (WHC) of SPHIW was measured by saturating the soil after placing it on a filter paper on a shallow pan of water. Later, the soil was allowed to drain in a water-saturated atmosphere until the drainage was complete and the water content was determined. The contents of total metals (Ni, Cd, Co, Cr, Pb, Fe, Zn and Mn) in the SPHIW were measured by digesting the SPHWI with aqua regia (HCl: HNO_3, 3:1 v/v) in an open flask digestion system as proposed by Chen and Ma (2001) and further measured on atomic absorption spectrophotometer [AAS (PerkinElmer, AAS 800, USA]. The physicochemical properties of SPHIW are illustrated in Table 1.

While collecting the samples of SPHIW from the arable field, the samples of same WW were also collected from the water channel irrigating this field. Wastewater samples (200 L) were stored in pre-washed (with 1% nitric acid) polyethylene bottles and stored at 4 °C. The WW was analyzed for pH and EC by using pH meter (model WTW 7110, Weilheim, Germany) and EC meter (BANTE, DDS-12DW, China) as explained in OMA (1990). Similarly, the contents of organic matter and $CaCO_3$ in WW were measured according to the methods described in

Table 1
Properties of experimental soil and wastewater (WW). The metals from soil were extracted with aqua regia (HCl: HNO_3, 3:1 v/v) (Chen and Ma, 2001). While, the heavy metal from WW were extracted with concentrated HNO_3 [APHA (American Public Health Association), 2005].

Properties	Soil	Units	Sewage Water	Units
Texture	Clay Loam	–	–	–
Soil order	Aridisols	–	–	–
Sand	16	%	–	–
Silt	41	%	–	–
Clay	43	%	–	–
OM	3.8	%	0.09	%
WHC[a]	520	g Kg^{-1}	–	–
EC	4.1	dS m^{-1}	1.8	dS m^{-1}
Lime	2.9	%	0.19	(%)
pH	8.2	–	7.9	–
Fe	321.8	mg kg^{-1}	2.19	mg L^{-1}
Zn	59.3	mg kg^{-1}	0.29	mg L^{-1}
Mn	62.8	mg kg^{-1}	7.9	mg L^{-1}
Co	24.6	mg kg^{-1}	0.12	mg L^{-1}
Cr	21.9	mg kg^{-1}	0.09	mg L^{-1}
Ni	58.1	mg kg^{-1}	0.29	mg L^{-1}
Cd	31.7	mg kg^{-1}	0.35	mg L^{-1}
Pb	64.4	mg kg^{-1}	0.69	mg L^{-1}

[a] Water holding capacity.