Carpathian Journal of Earth and Environmental Sciences, February 2021, Vol. 16, No. 1, p. 223 – 236; DOI:10.26471/cjees/2021/016/169

THE EFFECTS OF THE APPLICATIONS OF ZEOLITE AND BIOCHAR TO THE SOILS IRRIGATED WITH TREATED WASTEWATER ON THE HEAVY METAL CONCENTRATIONS OF THE SOILS AND LEACHING WATERS FROM THE SOILS

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Abstract: The reuse of wastewaters for agricultural irrigation is a method used in arid and semi-arid regions. The heavy metal accumulation in soils caused by wastewaters and the heavy metals transported by the waters leaching into the underground from these soils are important environmental issues. The study investigates the effects of Biochar (Bc) and Zeolite (Zt) applications on the heavy metal accumulation in soils (entisol and vertisol) that were irrigated with treated urban wastewater (TWW). The effects of Bc and Zt on the heavy metal concentrations of the leaching water (LW) from the soils were investigated as well. In the study, increasing doses of Bc (1%, 2%, and 4%) and Zt (5%, 10%, and 20%) were mixed into two soil classes of heavy- and fine-textured soils. The mixtures were irrigated with TWW at certain intervals. At the end of the trial, the chromium (Cr), iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), lead (Pb), and cadmium (Cd) contents of the samples collected from the soils and leaching irrigation waters were determined. The results revealed that Bc and Zt caused heavy metal accumulation in both soil classes, while they decreased the heavy metal concentrations of the LW. The adsorbents are commonly used as soil amendments and have been determined to cause heavy metal accumulation in soils but reduced the heavy metal concentrations in waters by serving as filters.

Keywords: Wastewater, İrrigation, Biochar, Zeolite, Heavy metals, Leaching water, Heavy metal mobility

1. INTRODUCTION

The increasing water consumption due to the increasing population adds to the growing importance of freshwater resources. The decreasing resources have necessitated the reuse of wastewaters in many sectors, especially in agriculture. Urban wastewaters are the leading reused wastewaters. They have become important water resources for agricultural irrigation especially in arid and semi-arid regions, which have limited water resources (Angin et al., 2005; Pham & Watanabe, 2017; Mojid et al., 2019). The agricultural, industrial, and domestic uses of treated wastewaters worldwide are 70%, 20%, and 10%, respectively (Kâtip, 2018). In addition to water shortage, wastewaters are used for their rich nutrient contents and contributions to product yield (Angın et al., 2005; Stevens et al., 2004; Al-Hamaiedeh & Bino, 2010). On the other hand, the use of wastewaters is not suitable in terms of sustainable agriculture and environmental health due to the toxic materials, high heavy metal concentrations, and pathogenic bacteria they contain. The wastewaters used for irrigation purposes negatively affect the physical and chemical properties of soils (Chen et al., 2004; Tarchouna et al., 2010). Long-term irrigation causes structural defects (Levy, 2011), heavy metal pollution (Asano & Pettygrove, 1987; Zavadil, 2009), and salinity problems (Muyen et al., 2011).

The most important environmental impact of wastewaters that are used for irrigation is the heavy metal accumulation in soils. It has been determined by studies that some heavy metals are transported along with sediment transport as a result of surface flow or percolation (Tudorache & Marin, 2012), Long-term irrigation leads to high concentrations of heavy metal accumulation in soil profiles (Khan et al., 2008; Houda et al., 2016; Nzediegwu et al., 2019). Various researchers have investigated the removal of heavy metals from wastewaters, immobilization of heavy metals in soils, and the prevention of their transport to plants. In their study on an area that had been irrigated with wastewaters for 20 years, Mkhinini et al., (2020) determined that heavy metals such as Cd, Cu, Zn, and Ni accumulated in the soil and enzymatic activity was reduced. Another study reported that significant levels of iron, zinc, copper, and manganese accumulated in the vegetables collected from an area that had been irrigated with wastewater (Arora et al., 2008). Another study showed that heavy metals accumulated in the soils and harvested plants in an area irrigated with wastewater (Massaquoi et al., 2015). Among the heavy metals accumulated in soils, arsenic, cadmium, chromium, lead, and mercury are of prior importance due to their high toxicity levels and, thus, the threat they pose for human health (Tchounwou et al., 2012). Plants take up heavy metals accumulated in soils, which are then transferred to the human body. In addition, heavy metals are mixed with groundwaters by percolation or transported by runoff, which leads to the pollution of ground and surface waters. Today, various organic or inorganic materials are used for the immobilization of heavy metals. These materials help the retention of some heavy metals in soils. The adsorption method is frequently employed to reduce heavy metal concentrations in solutions (Wang et al., 2013).

Biochar and Zeolite are the most widely used adsorbents in adsorption methods. Biochar and natural zeolites are soil amendments used for the improvement of the hydrophysical properties of soils and yields (Glisic et al., 2009; Lehmann & Joseph, 2009; Ahmed et al., 2016). The adsorbents are also used for the immobilization of toxic elements (Chlopecka & Adriano 1996; Terzano et al., 2005; Mahabadi et al., 2007). In their study, Contin et al., (2019) determined that the addition of natural zeolite to soils reduced the mobility of potentially toxic elements. Dang et al., (2019) found that biochar and biochar+apatite mixture reduced the exchangeable forms of cadmium, lead, and zinc. In light of the literature, the effects of biochar and natural zeolite on the heavy metal accumulation in soils and the heavy metal concentrations of the leaching irrigation waters from the soils were investigated. Thus, the study analyzes both accumulation and leachage. The study investigates the effects of biochar (Bc) and zeolite (Zt) on the heavy metal accumulation in the soils (entisol and vertisol) that were irrigated with treated urban wastewater (TWW). In addition, the study examines the effects of the adsorbents on the heavy metal concentrations of the leaching waters from the soils due to irrigation.

2. MATERIALS AND METHOD

2.1. Study materials and procedure

The study was carried out in the Soil Physics Laboratory of the Bingöl University Faculty of Agriculture, Bingöl, Turkey, between March 2020 and July 2020. The main materials of the study comprised two classes of sandy and clayey soils, two adsorbents serving as soil amendments (Zeolite and Biochar), and treated urban wastewaters.

Soils (S1** & **S2): The soils were collected from an area in Bingöl Plain in which irrigated agriculture is highly common. The soils were transferred to the laboratory and prepared for the trial (cleaning, grinding, sieving using a 2-mm sieve, etc.). The soils were classified according to the Soil Taxonomy-USDA (2014) prepared by Demir (2016).

Biochar (Bc) and Zeolite (Zt): The Zeolite used in the study was purchased from a commercial company (Eren Farm Organizations, 2019. www.n11.com/magaza/erenziraat.com). The natural zeolites used in the study are extracted from the mine deposits in Bigadiç district of Çanakkale province. These zeolites contain more than 75% clinoptilolite-heulandite and analcime, smectite, opal-CT, quartz and feldspar minerals (Köktürk & Gümüş, 1995).The natural zeolite was analyzed under laboratory conditions to determine its general properties. Biochar was the other adsorbent that was used in the trial and obtained by the pyrolysis of walnut shells at 500°C.

Treated Wastewater (TWW): The wastewater used for irrigation was obtained from the wastewater treatment facility located in Bingöl Plain. In the facility, the wastewaters are only physically treated and no chemical or biological treatments are carried out. The wastewaters from the facility were analyzed in the laboratory. Table 1 shows the general properties of the adsorbents, wastewaters, and soils in the study.

Soils containing increasing doses of Zt and Bc were prepared for both soil classes (S1 and S2). For this purpose, 5%, 10%, and 20% zeolite-containing soils and 1%, 2%, and 4% biocarbon-containing soils were prepared on a weight basis. In addition, control applications were carried out for both soil classes. The mixtures were emptied in three repetitions into the experimental containers that are detailed in Figure 1.

The containers were kept at the field capacity moisture level using pure water for 15 days to achieve a natural soil pore structure. Then, the soils were irrigated with wastewater at certain intervals. To determine the irrigation water requirements, the

Table 1. The general characteristics of the soils, wastewaters, and adsorbents in the study.

		Soil 1	Soil 2	Wastewater	Biochar	Zeolite
Sand (%)		27.0	58.0			
Silt (%)		25.0	24.6			
Clay (%)		48.0	17.4			
Texture Class		C	SL			
Db (gr/cm3)		1.22	1.49			
FC (%)		42.9	18.2			
WP (%)		17.0	14.0			
pH		7.2	7.0	7.75	9.5	9.1
EC (µS/cm)		617.5	176.4	1529.0	1.825	225.5
$CaCO_3$ (%)		0.2	0.1	-	-	2.1
OM (%)		2.4	2.3	-	77.5	0.17
CEC (cmol/kg)		41.5	31.6	-	35.5	48.5
Cr (ppb)		627.14	595.58	10.77		
Fe (ppb)		420.55	398.85	11.66		
Co (ppb)		305.84	185.75	0.012		
Ni (ppb)		681.22	225.48	174.57		
Cu (ppb)		146.36	126.75	171.36		
Cd (ppb)		1.84	1.05	121.66		
Pb (ppb)		265.85	368.75	370.11		
Soil Taxon.	**Ordo**	Vertisol	Entisol			
	Subordo	Xerert	Fluvents			
	Great Group	Haploxererts	Xerofluvents			

Db: Bulk density, FC: Field capacity, WP: Wilting point, EC, Electirical conductivty, OM: Organic matter, CEC:Cation Exchange capacity, Cr: Cromium, Fe:İron, Co: Cobalt, Ni: Nickel, Cu: Cupper, Cd: Cadmium, Pb:Lead

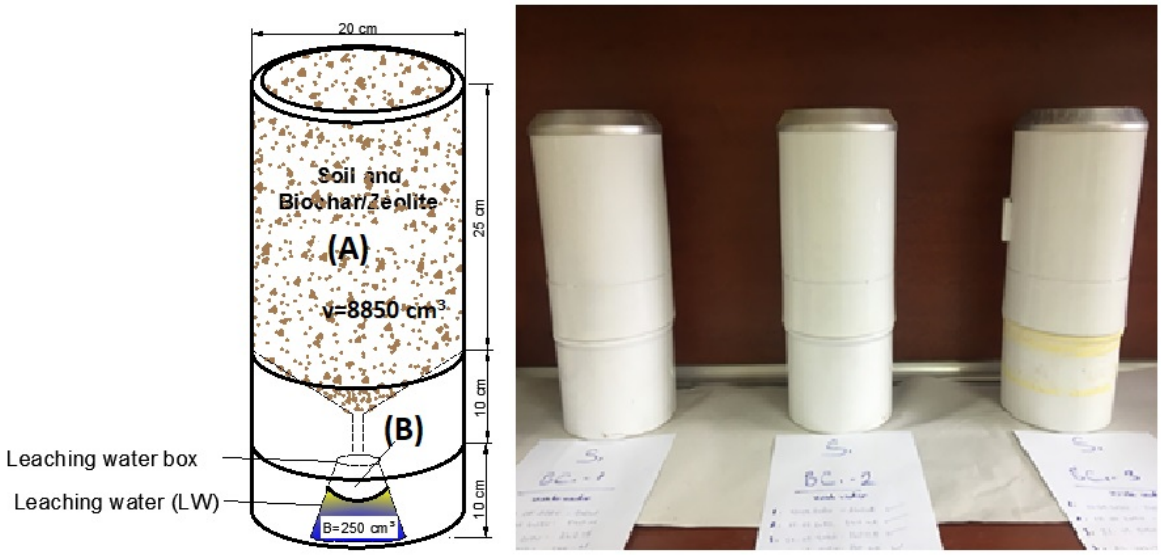

Figure 1. Experiment plots used in the study and drawing details (A: soil container, B: Leaching water box)

inflow and outflow waters to each extra setup (container) for each container were measured. Thus, the irrigation water amounts for each subject were determined. In the calculation of the irrigation water amounts, 120% of the required water was applied considering the irrigation water amount that will be collected (Yurtseven & Baran, 1998). Accordingly, 100±25 ml of water (percolating surface water) was collected from the experimental soils after each irrigation. Each application has different water holding capacity due to the different Bc and Zt doses it contains. Therefore, different amounts of leaching water were collected from each application (100 ± 25 ml). It is predicted that about 100 ml is sufficient for the analysis of the leaching water. In the vegetable and grain irrigation in Bingöl region, irrigation is carried out approximately 10-15 times in a production season (effect of temperature and plant water consumption). In the study conducted by Demir & Şahin (2020) with wastewater in Bingöl, tomato plant was irrigated 12 times. Therefore, 12 irrigation times were done with wastewater in this study. After irrigation, the waters collected for each setup were kept under appropriate conditions and mixed to create an analysis sample at the end of the trial. Thus, the irrigation waters that were collected after 12 irrigations were mixed to obtain a single sample. Moreover, the soil samples that were collected from each setup were analyzed to determine the heavy metal accumulation in the soils at the end of the trial.

2.2. Analyses of the Soils, Adsorbents, and Waters

The grain size distributions of the soils were determined by following the method proposed by Gee & Bauder (1986). Cation exchange capacities (CEC), pH ($pH_{1:2.5}$), electrical conductivity values, ($EC_{1:2.5}$), organic material contents (OM), and lime contents ($CaCO_3$) were determined using the methods proposed by Page et al. (1982). The field capacity (FC), wilting point (WP), and bulk density properties of the soils were determined in accordance with Tinsley (1967). The heavy metal contents of the soils were determined using an inductively-coupled plasma mass spectrometry (ICP-MS) device and HNO_3:HCl (3:1) acid mixture (Chen & Ma, 2001). The heavy metal contents of the wastewaters were determined in accordance with Greenberg et al. (1985).

2.3. Statistical analysis

The study was carried out in three repetitions. The SPSS 11.5 package program was used for the statistical analyses of the effects of the adsorbents on heavy metal concentrations. All data were analyzed using one-way variance analysis (ANOVA). The Duncan's test was used to determine the significant differences between the application factors ($P < 0.05$).

3. RESULTS AND DISCUSSION

3.1. The Effects of the Zeolite and Biochar Additives on the Heavy Metal Contents of the Leaching Waters from the Soils

The increasing doses of Zt and Bc that were mixed into the soil significantly affected the Cr contents of the leaching waters from the TWW-irrigated soils ($p < 0.05$). The chromium content decreased with increasing adsorbent addition to the soil (Table 2). Compared with the non-additive-mixed soil, Zt and Bc reduced the Cr amount in the leaching water. The same results were obtained in both soil classes (S1 and S2). Examining the differences between the applications in Table 2 reveals that the Bc4 application had the highest effect. The highest concentration was obtained in the control application. The Fe concentrations in the leaching waters were also significantly affected by the Zt and Bc applications ($p < 0.05$). The highest concentrations were obtained in the control applications, while the lowest Fe contents were obtained with the Bc4 application in both soil classes. The Fe amount decreased with increasing Bc doses in the S1 and S2 soil classes. On the other hand, this was only achieved with the Zt application to the S2 soil class. There was no linear relationship between the Zt dose and Fe content of the leaching water. The Co contents of the LW that was collected from the S1 soil after a total of 12 irrigations with TWW were between 0.261 ppb and 3.714 ppb. There was a significant difference between the applications ($p < 0.05$). The lowest Co content was obtained with the Zt10 application, while the Bc1 application had the highest Co content. Here, the lack of a linear relationship between the increasing doses of applications and the Co content of LW was noteworthy. In other words, unlike the Cr and Fe elements, there were no linear relationships between the increasing Zt and Bc doses and Co content. On the other hand, there was a linear relationship between the Co content and increasing doses of Zt and Bc in the trial with the S2 soil. When the control application is ignored, the Co contents of the LW decreased with the increasing doses of Zt and Bc applications to the soil. Moreover, there were significant differences between the applications ($p < 0.05$). The lowest Co content was obtained with the Bc4 application, while the Zt5 application had the highest Co content. The Ni content of the LW that was collected after the irrigation of the S1 soil was significantly affected by the mixing of Zt and Bc into the soil ($p < 0.05$). The Ni contents of the analyzed water were between 20.250 ppb and 103.191 ppb. The highest value was obtained in the control application, while the Bc4 application had the highest value. The Ni values revealed that (Table 2; S1) the Ni content of the LW decreased with increasing doses. Compared with the control application, the Ni amounts were significantly reduced in the Bc4 and Zt20 applications. The analyses of the LW from the S2 soil revealed that the Ni contents ranged from 4.823 ppb to 53.964 ppb. The lowest value was obtained in the Bc2 application, while the control application had the highest value. As seen in Table 2, the applications were significantly different ($p < 0.05$). There was no distinct relationship between the doses mixed into the soil and Ni contents. The Cu contents of the LW collected from the TWW-irrigated S1 soil ranged from 0.009 ppb to 3.241 ppb.

Table 2. The effects of the applications of zeolite and biochar to Vertisol and Entisol soils on the leaching heavy metal contents from the soils

Soil Type	Treatments	Heavy metals detected in leaching water (LW) leached from soils irrigated with treated wastewater (TWW)*						
		Cr (ppb)	Fe (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Cd (ppb)	Pb (ppb)
S1	Non treat.	0,382 ± 0,005e	22,109 ± 0,360f	1,496 ± 0,027c	103,191 ± 1,663f	3,241 ± 0,659e	1,955 ± 0,130c	30,519 ± 0,601d
	Zt5	0,381 ± 0,005e	14,115 ± 0,564c	0,717 ± 0,037b	73,399 ± 1,168d	3,064 ± 0,295cd	2,199 ± 0,130cd	13,793 ± 1,329c
	Zt10	0,285 ± 0,004b	10,984 ± 1,36b	0,261 ± 0,020a	30,590 ± 0,788b	2,756 ± 0,098c	0,957 ± 0,129b	0,064 ±0,055a
	Zt20	0,158 ± 0,003a	12,811 ± 0,917c	3,087 ± 0,117e	21,489 ± 0,914a	3,736 ± 0,901d	0,880 ± 0,132b	0,029 ± 0,025a
	Bc1	0,370 ± 0,004d	19,577 ± 1,035e	3,714 ± 0,084f	99,544 ± 1,153e	2,516 ± 0,118c	2,942 ± 0,124e	12,882 ± 0,499c
	Bc2	0,163 ± 0,001a	16,302 ± 0,891d	1,947 ± 0,096d	68,197 ± 1,358c	1,421 ± 0,266b	2,498 ± 0,205d	13,429 ± 0,670c
	Bc4	0,157 ± 0,005a	8,611 ± 0,454a	0,319 ± 0,028a	20,250 ± 0,978a	0,009 ± 0,088a	0,329 ± 0,1305a	10,727 ± 0,799b
S2	Non treat.	0,340 ± 0,01e	55,056 ± 1,392f	2,729 ± 0,041b	53,964 ± 0,699f	8,342 ± 0,401f	0,368 ± 0,015f	10,45 ± 0,667bc
	Zt5	0,312 ± 0,004d	44,519 ± 0,831d	3,291 ± 0,226c	33,008 ± 0,735e	7,765 ± 0,401e	0,308 ± 0,011e	11,467 ± 0,332c
	Zt10	0,241 ± 0,013c	31,309 ± 0,475c	2,446 ± 0,188b	32,888 ± 2,14e	9,048 ± 0,344g	0,055 ± 0,012a	11,518 ± 1,187c
	Zt20	0,131 ± 0,01b	23,659 ± 1,139b	1,373 ± 0,105a	10,998 ± 1,698c	6,111 ± 0,251d	0,051 ± 0,002a	10,06 ± 0,508b
	Bc1	0,121 ± 0,005b	34,302 ± 1,203d	3,149 ± 0,432c	26,223 ± 0,958d	3,953 ± 0,137b	0,271 ± 0,019d	11,363 ± 0,371c
	Bc2	0,119 ± 0,005b	21,849 ± 1,183b	2,447 ± 0,15b	4,823 ± 0,319a	4,950 ± 0,114c	0,176 ± 0,013c	10,051 ± 0,492b
	Bc4	0,032 ± 0,006a	15,355 ± 0,799a	1,064 ± 0,137a	8,725 ± 0,302b	1,836 ± 0,198a	0,092 ± 0,017b	8,91 ± 0,109a

*The letters show that the difference between the applications is statistically significant ($p < 0.05$).

The Bc4 application had the lowest Cu amount, while the highest Cu amount was obtained with the control application. The Cu contents decreased with increasing doses and there were significant differences between the applications in terms of the Cu contents ($p < 0.05$). As in the case of the Ni element, the Cu amount was significantly reduced in the Bc4 application when compared with the control application. On the other hand, it can be concluded that Zt and Bc adsorbed the Cu content to high degrees considering the Cu content of the TWW (171.36 ppb). Although there was no distinctly linear relationship between the application doses and Cu contents, there were significant differences between the Cu contents of the LW obtained from the S2 soil. The highest value was obtained with the Zt10 application (9.048 ppb), while the lowest value was detected, again, in the Bc4 application (1.836 ppb). Cd was another element identified in the LW and the Cd contents of the S1 soil were between 0.329 ppb (Bc4) and 2.942 ppb (Bc1). The Cd contents of the S2 soil were between 0.051 ppb (Zt20) and 0.368 ppb (control). Considering the Cd concentration in the TWW, the Cd content of the LW was significantly reduced. The lowest Pb concentration in the LW obtained from the S1 soil was obtained in the Zt20 application, while the highest concentration was obtained in the control application in which no materials were mixed into the soil. There were significant differences between the applications ($p<0.05$). Furthermore, there was a negative relationship between the application doses of Zt and Pb contents (control>Zt5>Zt10>Zt20). However, no such relationship was observed in the Bc applications (control>Bc2>Bc1>Bc4). The Pb concentrations obtained from the S2 soil were between 8.91 ppb (Bc4) and 11.518 ppb (Zt10).

3.2. The Effects of the Zeolite and Biochar Additives on the Heavy Metal Accumulation in the Soils

The heavy metal contents (Cr, Fe, Co, Ni, Cu, Cd, and Pb) of the two soil classes (S1 and S2) that were irrigated 12 times with TWW were determined. Table 3 shows the values obtained for each element after the analyses. There were significant differences between the heavy metal amounts that were retained in the soils in all applications. The Cr amount in the applications to the S1 soil significantly increased ($p>0.05$) compared with the control application. The lowest accumulation was detected in the control application (0.76 ppm), while the highest accumulation was obtained with the Bc2 (1.293 ppm) application. The Bc2 and Zt10 applications were in the same statistical group. There were no linear relationships between the increasing Zt and Bc doses and Cr accumulation in the S1 soil. A similar case was also true in the applications to the S2 soil. The Cr accumulation amounts in the S2 soil were between 0.786 ppm and 0.982 ppm. The highest accumulation was obtained in the Bc4 application, while the Bc1 application resulted in the lowest accumulation. The Fe contents in the S1 soil ranged from 446.449 ppm to 736.540 ppm. As was the case of Cr, the mixing of Zt and Bc into the soil affected the Fe accumulation, but no positive or negative accumulations occurred due to the increasing doses of the applications. The lowest accumulation was determined in the control application, while the highest accumulation was determined in the Zt10 application. The Fe accumulation in the S2 soil ranged from 757.737 ppm to 893.407 ppm. In the same manner as the S1 soil, the lowest accumulation was determined in the control application. Different from the S1 soil, the highest accumulation was determined in the Bc4 application. Again, unlike the S1 soil, there was a positive relationship between accumulation and increasing Bc doses (Control<Bc1<Bc2<Bc4). Considering the Co contents of the soils, the lowest accumulation in the S1 soil was 0.342 ppm and obtained with the control application, while the highest accumulation was 0.602 ppm and obtained with the Bc2 application. The Z10, Bc2, and Bc4 applications were in the same statistical group. The lowest Co accumulation in the S2 soil was obtained with the Bc1 application, while the Zt10 application resulted in the highest Co accumulation. In common in the S1 and S2 soils, the Zt10 accumulation had attracted attention for causing the highest accumulation. The Ni accumulations in the soils ranged from 0.955 ppm (control) to 1.711 ppm (Zt20) in the S1 soil and from 0.846 ppm (Bc1) to 1.363 ppm (Bc4) in the S2 soil. In the applications to both soil classes, there was only a relationship between the Ni accumulation in the S1 soil and Zt applications (control<Zt5<Zt10<Zt20). There were no relationships between the Ni accumulation and increasing doses of other applications. The addition of the increasing doses of Zt to the S1 soil resulted in the accumulation of Ni. The irrigations with the TWW led to Cu amounts ranging from 0.291 ppm to 1.079 ppm in the S1 soil and from 0.446 ppm to 0.986 ppm in the S2 soil. The lowest Cu contents in the S1 and S2 soils were obtained with the control and Bc2 applications, respectively, while the highest Cu contents in both soil classes were obtained with the Bc4 application. In both soil classes, the Zt and Bc applications significantly affected the Cu contents and there were significant differences between the

Table 3. The Heavy Metal Concentrations Caused by the Applications of Different Doses of Zeolite and Biochar to Wastewater-Irrigated Vertisol and Entisol Soils

Soil Type	Treatments	Heavy metals detected in soils irrigated with treated wastewater (TWW)*						
		Cr (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Cd (ppm)	Pb (ppm)
S1	Non-treat.	0,76 ± 0,005a	446,449 ± 0,364a	0,342 ± 0,003a	0,955 ± 0,010a	0,291 ± 0,011a	0,012 ± 0,001a	2,757 ± 0,039a
	Zt5	0,996 ± 0,006c	589,208 ± 0,242c	0,499 ± 0,003c	1,355 ± 0,006c	0,528 ± 0,010d	0,021 ± 0,001d	4,218 ± 0,008d
	Zt10	1,277 ± 0,018e	736,540 ± 0,028g	0,597 ± 0,005e	1,634 ± 0,025d	0,495 ± 0,006c	0,018 ± 0,001c	4,546 ± 0,017f
	Zt20	1,010 ± 0,011c	616,063 ± 9,59d	0,545 ± 0,006d	1,711 ± 0,035e	0,573 ± 0,007e	0,022 ± 0,001e	4,039 ± 0,039c
	Bc1	0,855 ± 0,010b	494,110 ± 6,832b	0,442 ± 0,002b	1,276 ± 0,019b	0,411 ± 0,001b	0,015 ± 0,001b	3,146 ± 0,016b
	Bc2	1,293 ± 0,007e	724,586 ± 6,91f	0,602 ± 0,009e	1,633 ± 0,004d	0,511 ± 0,001cd	0,018 ± 0,001c	4,318 ± 0,015e
	Bc4	1,248 ± 0,022d	695,694 ± 6,435e	0,599 ± 0,012e	1,623 ± 0,001d	1,079 ± 0,040f	0,019 ± 0,001cd	4,782 ± 0,003g
S2	Non-treat.	0,929 ± 0,029cd	757,737 ± 12,067a	0,566 ± 0,005d	0,979 ± 0,004e	0,859 ± 0,008c	0,009 ± 0,001a	2,432 ± 0,013cd
	Zt5	0,911 ± 0,015c	850,395 ± 5,102cd	0,497 ± 0,005b	0,941 ± 0,004c	0,926 ± 0,005d	0,009 ± 0,001a	2,267 ± 0,037b
	Zt10	0,851 ± 0,040b	788,295 ± 16,131b	0,588 ± 0,011e	0,958 ± 0,009d	0,952 ± 0,003e	0,077 ± 0,057b	2,459 ± 0,006d
	Zt20	0,959 ± 0,029de	862,832 ± 17,160d	0,572 ± 0,004d	0,945 ± 0,002c	0,923 ± 0,009d	0,015 ± 0,001a	2,763 ± 0,032e
	Bc1	0,786 ± 0,016a	791,913 ± 7,939b	0,481 ± 0,006a	0,846 ± 0,005a	0,57 ± 0,002b	0,011 ± 0,001a	2,041 ± 0,055a
	Bc2	0,916 ± 0,005cd	831,752 ± 10,627c	0,497 ± 0,004b	0,878 ± 0,002b	0,446 ± 0,010a	0,011 ± 0,001a	2,385 ± 0,025c
	Bc4	0,982 ± 0,006f	893,407 ± 4,752e	0,51 ± 0,004c	1,363 ± 0,009f	0,968 ± 0,022e	0,013 ± 0,001a	4,264 ± 0,005f

*The letters show that the difference between the applications is statistically significant (p <0.05).

groups ($p>0.05$). The addition of the increasing doses of Bc to the S1 soil caused the accumulation of Cu. The Cd contents of the S1 soil were between 0.012 ppm and 0.022 ppm. The Cd contents of the S2 soil were between 0.009 ppm and 0.077 ppm. The Cd accumulation in the S1 soil significantly increased with the Zt and Bc applications compared with the control application ($p<0.05$). On the other hand, in the S2 soil, which has a higher infiltration rate than the S1 soil, all applications were in the same statistical group, except for the Zt10 application. In other words, the Zt and Bc applications did not have any effect on Cd accumulation, except for the Zt10 application. As was the case for other elements, the Pb contents of the soils were affected by the Zt and Bc applications. The lowest Pb content in the S1 soil was obtained in the control application (2.757 ppm), while the Bc4 application resulted in the highest Pb content (4.782 ppm). According to the data given in Table 3, the increasing doses of Bc applications to the S1 soil caused Pb accumulation (control>Bc1>Bc2>Bc4). However, the case in the S2 soil was different from that in the S1 soil. The lowest Pb content in this soil was obtained with the Bc1 application (2.041 ppm), while the highest Pb content was obtained with the Bc4 application.

The heavy metal accumulation in the TWW-irrigated S1 and S2 soils and heavy metal contents of the LW from the soils were significantly affected by the Zt and Bc applications to the soils. Compared with the control application, the Cr accumulation after 12 irrigations increased with the addition of Zt and Bc to the soils (Fig.1). The effects of both materials on the Cr accumulation were statistically at the same level. On the other hand, the Cr contents of the LW decreased after the applications of Zt and Bc. The application of Bc was more effective on the decrease in the Cr concentration than the application of Zt ($p<0.05$). The LW from the control application had the highest Cr content, followed by the Cr contents of the LW from Zt and Bc, respectively (Fig 2). Cr is a heavy metal posing serious threats for human, animal, and plant health due to agricultural, mining, and other industrial wastes (Shanker et al., 2005; Dehghani et al., 2016). As good adsorbents (Wang et al., 2009; Chen et al., 2015), Zt and Bc caused Cr accumulation in the soils and decreased the Cr concentrations of the LW.

In addition to various elements and minerals, wastewaters contain high levels of Fe, Co, and Ni. These elements can accumulate in soils, be transferred to plants, and, then to other living beings. Although wastewaters contain lower levels of these elements, irrigations can lead to the accumulation of these elements in soils (Wuana & Okieimen, 2011). In terms of their accumulation in the soils in our study, the effects of Zt and Bc on Fe, Co, and Ni were at the same level. The retention of these elements was affected at the same statistical level by both adsorbents. On the other hand, the concentrations of these elements in the LW were affected to varying degrees. The Fe concentration of the LW was more affected by the Bc application than the Zt application. In other words, the Fe contents of the LW from the Bc-mixed soils were lower than those of the LW from the Zt-mixed soils. As shown in Table 2, the decrease in the Fe amounts in the LW with increasing doses agrees with our findings. The adsorbents used in the trial caused Co accumulation in the soils but did not have any effect on its concentration in the LW when compared with the control application. There were no significant differences between the applications. The results revealed that Ni was retained in the soil by the adsorbents. There was a significant accumulation compared with the control application. The adsorbents were not statistically different from each other. The Ni concentrations of the LW decreased at the same level after the Zt and Bc applications. The Cu and Cd contents after the irrigations of the soils were not affected by the applications of Zt and Bc. The effects of the adsorbents on the Cu and Cd accumulation were in the same statistical group as that of the control application. In other words, there were no statistically significant differences between the groups. On the other hand, the Cu content of the LW decreased with the Zt and Bc applications. The effects of Zt and Bc on the Cu contents of the LW were the same as each other. The effects of Zt and Bc on the Cd contents of the LW were not statistically significant when compared with the control application. The applications of Zt and Bc to the soils caused Pb accumulation and their effects on the Pb accumulation were different from each other (control<Zt<Bc; $p<0.05$). On the contrary, the Pb content of the LW decreased with the applications of Zt and Bc and the effects of the applications of Zt and Bc were statistically at the same level.

Zt and Bc are important adsorbents that are used for the immobilization of heavy metals in soils. Zeolites are commonly used in the adsorption of cadmium (Rao et al., 2006; Choi et al., 2016), lead, copper, and nickel (Chao et al., 2014; Yuna, 2016; Hong et al., 2019) due to their large grounce area and high adsorption ability (Erdem et al., 2004). Biochars are solid materials that are obtained with the thermochemical transformation of biomass in an oxygen-limited environment; they are rich in carbon (C) and have high porosity and surface load (Lehmann et al., 2011, Van Zwieten et al., 2010). Studies have shown that biocarbons are effective in

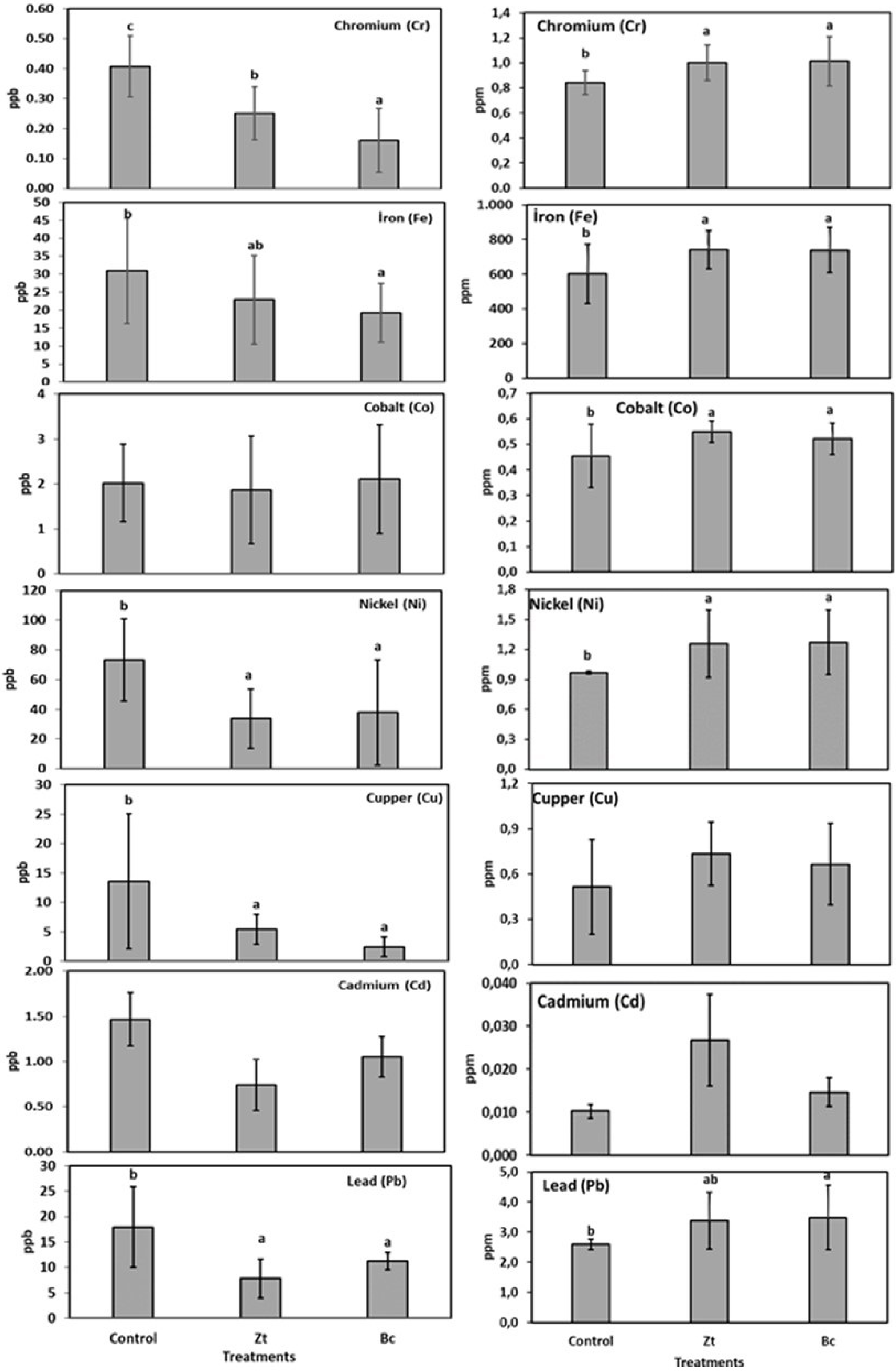

Figure 2. The effects of the Zeolite (Zt) and Biochar (Bc) applications to the wastewater-irrigated soils on the heavy metal contents of the soils (ppm) and leaching waters from the soils (ppb)

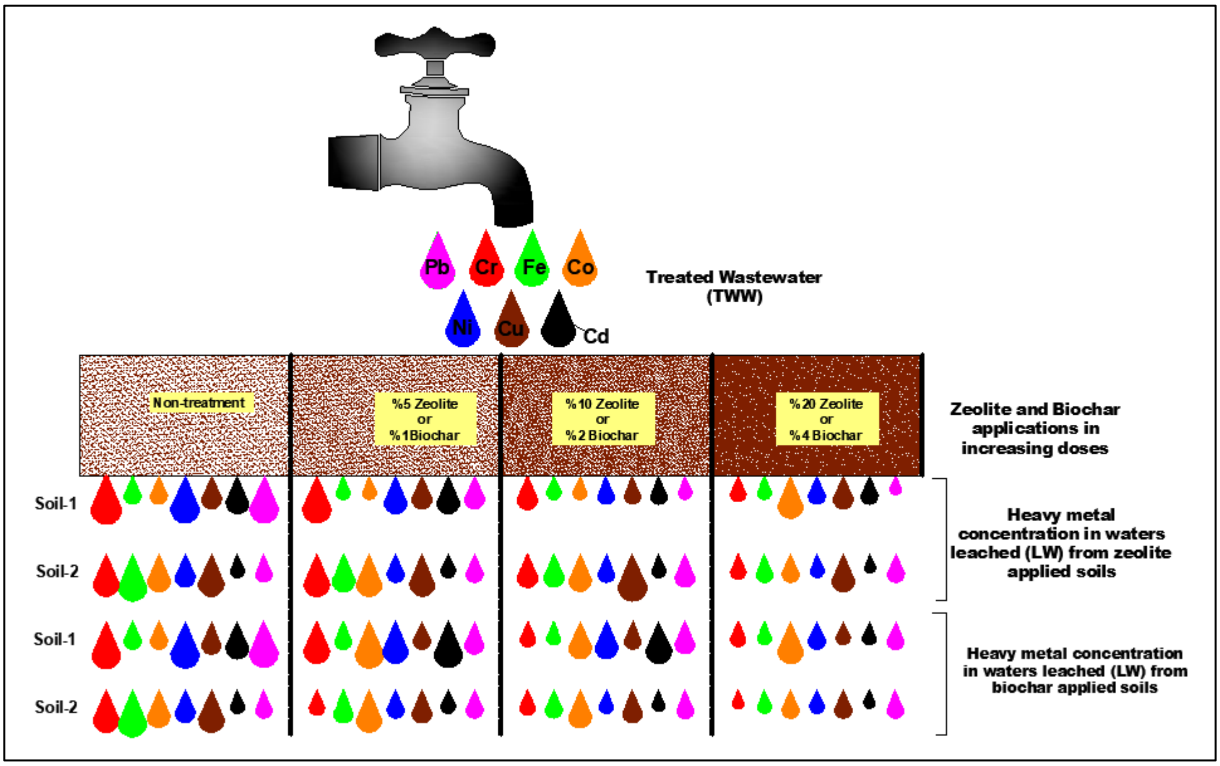

Figure 3. The General effect of Zeolite (Zt) and Biochar (Bc) on heavy metal concentration of leaching water in study

the removal of lead, cadmium (Mohan et al., 2007), mercury (Kong et al., 2011), copper, and zinc (Chen et al., 2011). However, the zeolitic tuffs used are characterized by a high content of zeolites with the presence of clinoptilolite and have a reduced mobility for Pb and Cd, especially due to Cu and Zn. The cationic exchange capacity was increased by adding zeolites and organo-zeolitic materials to the contaminated soils. The cationic exchange capacity also has the immobilization of heavy metals undertaken by plants (Damian et al., 2013). In our study, the Cr, Fe, Co, Ni, Cd, Cu, and Pb concentrations in the TWW-irrigated soils were affected by the applications of Zt and Bc. The adsorbents added to the heavy metal accumulation in the soils due to their pore structures, surface areas, and load capacities. The heavy metal contents of the LW from the same soils were also affected by the adsorbents. Compared with the control application, both Zt and Bc reduced the heavy metal concentrations in the LW. The results were observed for both soil classes, which have different physiochemical properties. This suggests that the waters mixing with the groundwaters were purified by the infiltration of the deeper levels. Various studies have reported reduced heavy metal mobility due to the use of Bcs. Cheng et al., (2006) reported that Bc (bamboo-derived biochar) adsorbed Cu, Hg, Ni, and Cr from soils and waters. In a similar study, in a soil polluted with Zn and Cd, Bc reduced the Zn and Cd contents of the water in the soil pores by 300- and 45-fold, respectively (Beesley et al., 2010). Namgay et al., (2010) reported that the extractable As and Zn concentrations in soil increased with the application of Bc, while the extractable Pb concentration decreased, Cu concentration remained the same, and Cd concentration showed an inconsistent pattern. In our study, the Cu, Cd, and Pb elements in the S1 soil that was mixed with the increasing doses of Bc accumulated in the ascending order as follows: control<Bc1<Bc2<Bc4. The same relationship was not observed between the Bc doses and accumulations of the Cr, Fe, Co, and Ni elements. The same ordering was only observed in the Fe accumulation in the S2 soil. There were inconsistent relationships between Bc doses and elements, except for Fe. However, the differences between the Bc and control applications were statistically significant in both soil classes, except for Co and Cd ($p<0.05$). In other words, Bc caused higher levels of element accumulation in soils, except for Co and Cd (Fig. 1). Our results concur with the literature. In addition, Zt affected the concentrations of some heavy metals in the soils after irrigation, but only the Ni concentrations changed in proportion to the Zt doses in the trials in the S1 and S2 soils. In other words, the addition of the increasing doses of Zt to the S1 soil increased the accumulation of Ni (control<Zt5<Zt10<Zt20). No such relationship was observed for other elements (Table 2). The effects of

the adsorbents on the element accumulations in the soil were not significantly different, except for Pb (Fig. 2). In other words, the effects of Zt and Bc on the Cr, Fe, Co, and Ni accumulation were statistically at the same level, while Zt was less effective on Pb accumulation than Bc ($p<0.05$).

Heavy metals that accumulate in soils or transferred to soils with irrigation pose an environmental threat when mobilized by irrigation and drainage (Fig. 3) These elements can accumulate in the drainage waters and, then, mix with and pollute the groundwaters. Municipal wastewaters are important factors in the pollution of groundwaters. The water that is given to soil by irrigation passes through soil pores and mixes with groundwater due to percolation. The quality of the percolating surface water mixed with groundwater depends on the pollution level of both irrigation water and soil, (Howard & Livingstone, 2000; Slack et al. 2004; Bakıs & Tuncan, 2011). The organic materials mixing with the soils affect the vertical and horizontal water movement by changing the pore structure. Especially in soils with macropores, the horizontal wetting distance increases, while vertical wetting distance and infiltration rate decrease due to the effects of these materials (Demir & Doğan Demir, 2019; Demir et al., 2019). This leads to increased contact between the polluted waters and the surfaces of the particles in soils and higher immobilization of heavy metals, especially in sandy soils. The pH values of the Bc and Zt that were used in the trials were higher than those of the S1 and S2 soils. The increasing doses of these materials in the soil increase the pH of the environment. The increase in soil pH affects the immobilization of certain heavy metals (Medyńska-Juraszek & Ćwieląg-Piasecka, 2020). Thus, the additions of the increasing doses of Bc and Zt resulted in the accumulation of heavy metals in the soils.

4. CONCLUSION

The results of our study revealed that zeolite and biochar adsorbed the heavy metals in the soils and reduced their mobility. The heavy metals in the wastewaters that were applied during the trial to the soils that contained different doses of zeolite and biochar accumulated in the soils. On the other hand, the concentrations of the heavy metals in the leaching waters from the soil decreased compared with the control application. Thus,

1) In irrigations with wastewater, the heavy metal content of the water can accumulate in the soil due to biocarbon and zeolite and cause heavy metal pollution. If there are plants in the soil, the excess heavy metals in the soil can accumulate in these plants and negatively affect human health. Thus, the materials that are mixed into the soils for any given reason will worsen heavy metal accumulation in the soil if irrigated with wastewater.
2) The zeolite and biocarbon adsorbents reduced the heavy metal concentrations of the leaching waters from the soils by retaining the heavy metals in the soils. This can lead to cleaner underground water or prevent the transfer of heavy metals to deeper levels. Therefore, the these adsorbents can serve as natural filters.

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Received at: 30. 10. 2020
Revised at: 19. 02. 2021
Accepted for publication at: 22. 02. 2021
Published online at: 23. 02. 2021