Reducing Bioavailability of Some Heavy Metals in a Contaminated Soil Using Rice Straw Compost and Water Treatment Residuals

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ABSTRACT

The present work was carried out to evaluate the effectof rice straw compost, water treatment residuals (WTR), and their mixture (2:1 and 1:1 wet weight) on heavy metals immobilization in contaminated soils and plant growth of canola (*Brassica napus*). Composite surface soil samples were collected from agricultural farms of El-Mahla El-Kobra area, Gharbia Governorate, Egypt. This farm was continuously irrigated with drainage water that received raw wastewater more than 10 years. The results showed that the applications of WTR, rice compost and their mixture have significantly decreased the concentrations of lead (Pb), cadmium (Cd) and zinc (Zn) extracted from soils by DTPA- method as well as their concentrations in the root and shoot of canola plants grown in the contaminated soil compared with the control. The dry weight of canola plants were also significantly increased with the application WTR and compost treatments compared with the control. The addition of rice compost and WTR mixtures (2:1 or 1:1 wet weight ratio) at level of 10 g dry weight kg^{-1} dry soil gave the best reduction in the three heavy metals contents soils and in plant growth compared with other treatments. Thus, the interaction between rice straw compost and WTR had been successfully used to lower the bioavailability and increase the geochemical stability of the Pb, Cd and Zn in the contaminated soil and increasing the yield of canola, and also improve the efficiency of rice straw and WTR disposal.

Key Words: ***rice straw compost, water treatment residuals, heavy metals, contaminated soil, canola plant, recycling.***

INTRODUCTION

The discharge of industrial and municipal wastewater without treatment in drains of Zefta and No.5 in EL- Mehalla EL koberia area, Gharbia governorate, Egypt is becoming a problem for many farmers, because they use the drainage water from these drains for irrigating their lands (Mahmoud 2008). Heavy metal contamination of soil poses a major threat to human health and the environment. Toxic heavy metal contamination is prevalent within the surface soils at industrial sites (Huang *et al.* 1997).

Traditional approaches to remediation of toxic heavy metal contaminated soils are typically expensive, labor intensive, and environmentally inefficient. Chemical immobilization is an in site remediation method where inexpensive materials (e.g., fertilizer, waste products) are added to contaminated soil to reduce the solubility of heavy metal contaminates. Because contaminant solubility is related to its mobility and bioavailability, chemical immobilization may reduce environmental risk (Basta *et al.* 2001). The mobilization of metals in soils can however be minimized through chemical and biological immobilization using a range of soil amendments, such as organic wastes, compost and phosphate compounds (Bolan *et al.* 2003). Pierzynski and Schwab (1993) showed that the application of organic amendments (i.e., cattle or poultry manure) reduced soybean (*Glycine max*) tissue Zn concentrations grown in metal-contaminated soil. Mahmoud (2005) found that the addition of water treatment residuals (WTR) to contaminated soil reduced wheat (*Triticum aestivum*) tissue Zn, Cd, and Pb concentrations. Metal immobilization through precipitation and adsorption is considered a common mechanism to reduce the hazards of heavy metals in contaminated soils (Malakul *et al.* 1998). Mahmoud *et al.* (2009) found that the combinations of water treatment residuals and rice straw compost had improved yield of canola plant and soil properties. The addition of compost and WTR to decrease plant accumulation of heavy metals was chosen as an alternative to the traditional soil amendments. Therefore, the aim of this study was to use WTR and rice straw compost as soil amendments for remediation of heavy metals contaminated soil at El-Mahla El-Kobra area.

MATERIALS AND METHODS

Prevailing conditions of the studied soil

Composite surface (0-30 cm) soil samples were collected from the agricultural farms of El-Mahla El-Kobra area, Gharbia governorate, Egypt. This farm was continuously irrigated with drainage water from drain No (5) for a period of about 10 years. All factories of El-Mahla El-Kobra (textile, oil and soap, printing and chemicals) discharge their effluents into this drain The soil of this farm is considered contaminated with Zn, Ni, Pb, and Cd where their total concentrations exceeded 300, 350, 260 and 10 mg kg^{-1} soil respectively (EPA, 1993).

Table 1: Physical properties and chemical constituent of the studied soil, rice straw compost and WTR

Properties	Units	soil	Rice straw Compost	WTR
pH (soil paste extracts)		7.86	7.17	7.73
EC	dS m^{-1}	2.97	3.9	2.16
Ca^{++}	meq L^{-1}	6.8	12.4	75.1
Mg^{++}	meq L^{-1}	3.4	4.6	9.2
Na^{+}	meq L^{-1}	22.4	20.5	18.3
K^{+}	meq L^{-1}	0.87	3.9	0.9
Al^{+++}	meq L^{-1}			280.0
Cl^{-}	meq L^{-1}	8.5	33.2	23.8
HCO_3^{-}	meq L^{-1}	6.5	5.0	4.5
SO_4^{--}	meq L^{-1}		3.2	75.2
SAR		9.95	7.04	2.81
$CaCO_3$	%	2.55	1.8	1.76
O.M	%	0.93	42.0	5.44
Clay	%	60.92		63.2
Total heavy metals				
Cd	mg kg^{-1}	60.0	2.0	7.5
Zn	mg kg^{-1}	856.48	39.5	38.0
NI	mg kg^{-1}	1122.0	12.0	34.0
Pb	mg kg^{-1}	593.2	17.5	62.0

Accordingly, it could be concluded that irrigation with polluted drainage water led to accumulation of heavy metals (Zn, Ni, Pb, and Cd) in soil (Table 1).

The soil sample was air - dried and ground to pass a 2 mm sieve. Some chemical and physical analyses of soil were carried out according to Black *et al.* (1982) and Page et al. (1982) and the obtained results are shown in Table (1)

Experiment and Treatments

Canola (*Brassica napus*) plants were grown in pots in a completely randomized experimental design with five replicates. Each pot contained 6.5 kg soil that was collected from the farm at El-Mahla El-Kobra area, Gharbia governorate. The water treatment residual (WTR), rice compost, WTR + rice compost (1:1 wet weight ratio) and rice compost + WTR (2:1 wet weight ratio) were added at levels of 10 and 20 g on dry weight basis for kg air-dried soil and mixed thoroughly. Plant shoots and roots were harvested after 8 weeks from planting. Plant organs were washed with tap water then rinsed with distilled water and dried in an oven at 60-70 ^{0}C for 72 hr. The oven dry weight was recorded. After canola plants harvesting, the soil samples were collected and prepared for chemical analysis.

The compost used in this experiment was made of rice straw and animal wastes. Water treatment residuals (WTR) were collected from Kafer El-Sheikh water treatment plant. The properties of the used WTR and rice straw compost are given in Table (1).

Compost, WTR and soil Analysis

Ash of compost was determined in a muffle oven at 550 °C for 8 h, and organic matter was calculated as the difference between ash and dry weight (50% from. O.M was considered organic C) (AFNOR 1991). The pH and EC were determined in the extract of the water saturated compost and soil using pH and conductivity meter, respectively. Total concentration of heavy metals were measured by atomic absorption after wet digesting the air dried WTR, plant and rice compost digested with concentrated H_2SO_4 + H_2O_2 (Cotteine et al. 1982). Clay content of WTR and soil was measured by the international standard pipette methods using sodium hexameta-phosphate as dispersing agent according to Black (1982). The soluble cations (Na^{+} Mg^{++}, Ca^{++}, K^{+}) and anions (HCO_3^{-} and Cl^{-}) were determined in soil paste extract (Rhoades, 1954). The amount of organic carbon of soil was determined according to Walkely- Black method (Page *et al.,* 1982) .Organic matter was calculated by multiplying the organic carbon value by the Van Bemmelen of 1.724. Total carbonate was determined using the calcimeter method as $CaCO_3$ percent (Page *et al.,* 1982). The amount of available heavy metals were extracted from soil using DTPA methods (Cotteine *et al.,* 1982) and measured by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Immobilization of bioavailable heavy metals

The application of the studied amendment levels for WTR, compost and their mixture provided an effective and sustainable solution for remediation of contaminants in the experimental soil. Applications of WTR, rice compost and their mixture have significant decreases in the amount of DTPA- extractable Pb, Zn and Cd concentrations Table (2). However, there is no significant decrease in the compost at 20 g kg^{-1} soil treatments. The addition of WTR showed a relatively higher decreasing order as compared with rice compost effect on DTPA- extractable metals from soils. The reduction of extractable Pb, Zn and Cd concentrations were reached to 51%, 44% and 50%, respectively in the pots treated with 10 g kg^{-1} soil [2 compost: 1 WTR] compared with the non-treated soil (control).. The obtained results of DTPA-extract of Pb, Zn and Cd in the pots treated with the WTR and rice compost combinations at two levels were similar and higher significant compared with other treatments.

Uptake of heavy metals

Table (3) showed that heavy metals response to uptake and accumulation in either shoot or root tissues were a closely related to their corresponding reduction in the bioavailability contents in the experimental soil treatment as a result of applying WTR and rice compost, (Tables 2, Figure 1 and 2). However, addition of WTR showed a relatively higher decreasing order as compared with rice compost in the canola plant. This is more close with the obvious differentiations between both amendments for their immobilization efficiency of the studied heavy metals which was towards WTR at this experiment. The addition of rice compost and WTR (2:1 or 1:1 wet weight ratio) at level of 10 g dry weight kg^{-1} dry soil gave the best reduction in the three heavy metals studied compared other treatments. Soil amendments (WTR and rice compost) had a significant effect on the reduction of the three heavy metals for canola plants, especially in the pots treated with the WTR and rice compost combinations. Table (3) also showed that the beneficial effect of applied both amendments on reducing the biological metals uptake in tissues of plant shoots was more pronounced than roots. This is mainly due to the slowly translocation of such metals from roots to shoots.

Dry weight

Generally, the application of water treatment residuals (WTR) and rice compost increased markedly the dry weight of canola plants at application levels of 10 and 20 g kg^{-1} soil compared with the control (Figure 1and 2). High dry weight of canola plants with addition of 10g kg^{-1} soil [2 rice compost: 1 WTR:] compared with others treatments. The dry weight decreased with the addition of WTR and rice compost at 20 g kg^{-1} soil compared with the levels 10 g kg^{-1} soil. The relative increase (R.I %) of dry weight of canola plants ranged from 13.25% with WTR at 20 g kg^{-1} to 51.15% with the addition of 10g kg^{-1} soil [2 rice compost: 1 WTR:]. The relative increase of dry weight of canola plants differed significantly between the treatments (Fig.1and 2)

Table 2: DTPA extractable contents of Pb, Zn and Cd as affected by the applied soil amendments

Treatments	DTPA extractable contents (mg kg^{-1} soil)		
	Zn	**Cd**	**Pb**
Control	78.3	4.6	88.2
WTR_{10}	46.3	2.8	55.2
WTR_{20}	45.1	2.6	50.2
$Compost_{10}$	51.2	3.2	56.2
$Compost_{20}$	53.8	3.3	59.2
$C1W1_{10}$	43.2	2.4	45.2
$C1W1_{20}$	43.9	2.5	44.6
$C2W1_{10}$	43.6	2.3	43.2
$C2W1_{20}$	44.2	2.4	42.8
$L.S.D_{0.05}$	25.98	1.68	32.92

W1C1: WTR+ Compost (1w:1w), C2W1: Compost + WTR (2w:1w)

Table 3: Average tissue Cd, Zn and Pb concentrations of canola as affected by the applied soil amendments

Treatments	Metals uptake(mg kg^{-1} dry matter)					
	Cd		Zn		Pb	
	Shoot	Root	Shoot	Root	Shoot	Root
Control	87.3	118.6	279.16	318.27	187.23	203.62
WTR_{10}	22.7	60.2	168.31	208.22	153.36	187.23
WTR_{20}	23.6	57.4	153.82	209.21	148.20	173.62
$Compost_{10}$	33.6	62.7	172.12	213.24	156.27	192.10
$Compost_{20}$	27.8	63.4	183.21	219.18	154.64	196.24
$C1W1_{10}$	17.5	47.9	132.32	198.26	139.23	168.23
$C1W1_{20}$	18.32	49.7	142.62	186.23	138.62	165.14
$C2W1_{10}$	18.2	43.8	143.32	196.26	133.45	173.61
$L.S.D_{0.05}$	52.0	52.69	101.86	94.64	39.89	31.04

W1C1: WTR+ Compost (1w:1w), C2W1: Compost + WTR (2w:1w)

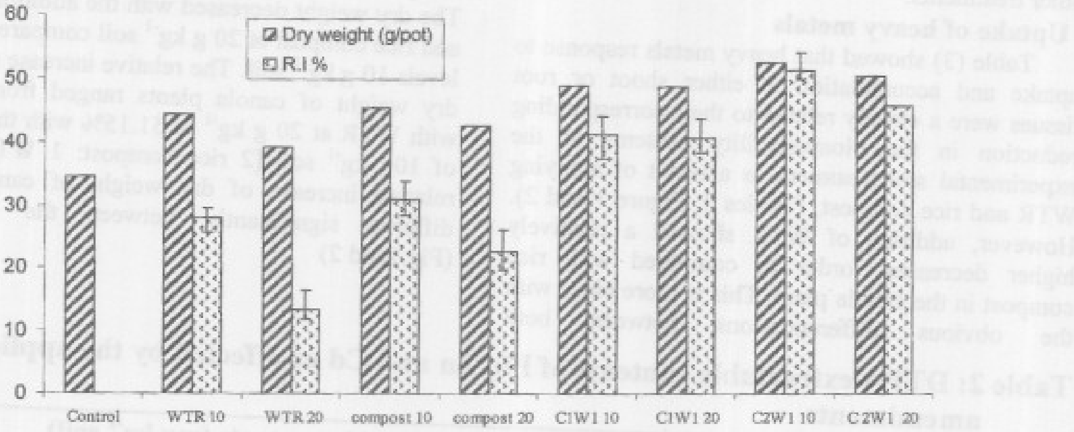

Fig.1: Dry weight and relative increase (R.I) of canola plants as affected by the applied soil amendments. Data points of relative increase are means and standard errors of three replications

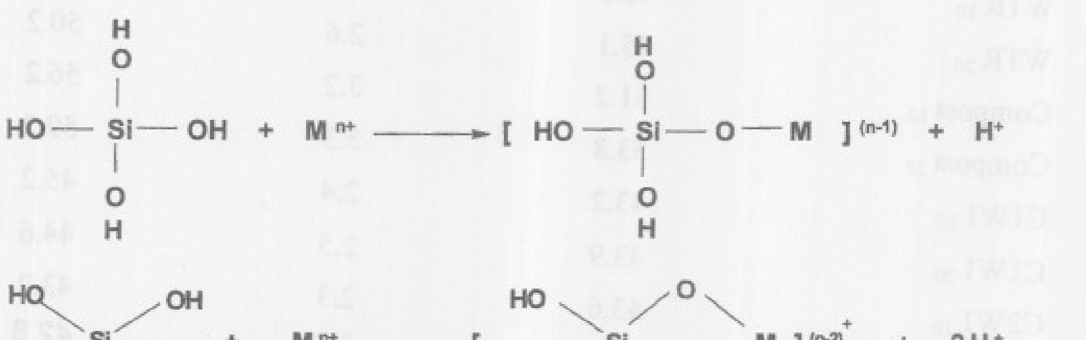

Fig. 2: Top: Complex formation between monosilicic acid and a cation, M^{n+}, in which n+ = the number of positive charges

Bottom: Chelating reaction between monosilicic acid and a cation, M^{n+} (Tan 2000)

Several studies showed that application of the polluted drainage water as an irrigation water led to accumulation of heavy metals in soils, especially in EL- Mehalla EL Koberia area, Gharbia governorate (Mahmoud and Abd El-Kader, 2008). Heavy metal contamination of soil poses a major threat to human health and the environment (Huang *et al.*, 1997).

The use of rice compost reduced Cd, Pb and Zn concentrations of root and shoot of canola plant grown in the studied soil. Pierzynski and Schwab (1993) reported that application of organic amendments (i.e., cattle or poultry manure) reduced soybean (*Glycine max*) tissue Zn concentrations grown in metal-contaminated soil. Bolan *et al* (2003) found that the compost application reduced extractable heavy metals. The metal adsorption increased with alkaline –stabilized biosolid compost addition to soil (Li *et al.* 2000). Addition of aged manure, straw, or compost can be an efficient method of adding organic matter to inorganic waste sites such as industrial wastes, planting wastes and mine tailings. Thus , the water holding capacity of waste is enhanced ,which helps with establishing trees, grasses or plants ,and the binding capacity of the soils is improved for immobilizing metals Eqs 1 and 2.

Metals binding to organics:

$$R\,OH + M^{2+} \rightleftharpoons R\,OM^{+} + H^{-} \quad (1)$$

$$R(OH)_2 + M^{2+} \rightleftharpoons (RO)_2M + 2H^{+} \quad (2)$$

Where: ROH represents the binding site on an organic material. Here, metal cations (M) are bound to particulate organic matter by bounding to phenolic, carboxylic, and hydroxyl bridging groups in soil humus, wastes or roots (Schnoor 2000). The decrease in the phytoavailability of metals in the presence of organic amendments is often attributed to increased complexation of the metal by organic constituents (Adriano 2001). The stability constant of 5.6 at pH 7.0 was reported for a Zn –soil- organic matter complex. Davies (1980) indicated that most of the Zn may have been adsorbed in the form of a Zn-humic acid complex. The interaction between humic acid and clay is made possible by metal or water bridging, called coadsorption. The metals such as Zn, Cd, and Pb can serve as bridge between the organic ligand (humic acid) and clay micelle as illustrated by the following reaction (Tan 2000):

Clay –metal – OOC–R–COO–metal–clay (3)

The compost used in the study employed rice straw as the bulking agent and its high silicon content. The metals such as Cd, Zn and Pb chelated by silica can function as bridges to bind clay particles. Soluble (Si) is present as monosilicic acid, $Si\,(OH)_4$ in a wide range from 2 to 9 (Ponn amperuma 1972) . The monosilicic acid is able to form complexes with metal ions as illustrated in Fig (III-5).

As the Pb, Cd and Zn concentrations had reduced in the root and shoot of canola plant grown in the studied soil by the application of WTR which is attributed to its high CEC, organic matter and clay (Table 1). This WTR used in the study contained 3640 1502 and 110.4 mg kg^{-1} for Al, Ca and Mg, respectively. This indicates the presence of the inorganic components which may be involved in the adsorption of heavy metals. Metal cations (Pb, Cd and Zn) are most tighty bound by those ions that form strong complex with OH groups on the surface of minerals also disturbances in plant mineral nutrition by competition with other nutrients (Siedlecka 1995).

The highest reduction of heavy metals occurred under level 10 g kg^{-1} soil [2 rice compost: 1 WTR]. The interaction between the compost and WTR on the on heavy metals immobilization was observed here. It might be due to lower the bioavailability and increase the geochemical stability of metal in the contaminated soil.

Since total Cd content of canola cultivated in the tested soil was about 205 mg kg^{-1} soil the plant can be defined as an hyperaccumulator as it accumulates at least 100 mg kg^{-1} soil of Cd in the plant when grown on metal – rich medium (Zavoda *et al.* 2001).

The observed increase in dry weight of canola plants in the WTR treatment at 10 or 20 mg kg^{-1} soil coincided with organic matter and soluble elements originated from WTR (Table 1) and also decreasing in the phytotoxic levels of available heavy metals (Table 2). Also, with the addition of rice compost the dry weight was increased. This may be attributed to the improving action of compost on the soil physical properties as well as nutrients status in the soil which enhance plant growth (EL.Sanat 2003). Dry weight of canola plants in the pots treated with rice compost at 20 g kg^{-1} was decreased compared with control. This could be due to increased elements originated from compost in soil solution which produced a condition of nutritional unbalance in plants particularly at relatively high levels of compost. Dry weight of canola plants increased with of WTR and rice compost mixed to soils coincided with improvement of the soil properties (Mahmoud *et al.* 2009).

CONCLUSION

From the technical point of view, heavy metals immobilization using mixture of the rice straw compost and water treatment residual (WTR) is an effective technique for reducing heavy metals solubility and mobility on a shot-term of use Combinations of WTR and rice straw compost could improve canola growth and the efficiency of organic wastes recycling.

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الملخص العربى

خفض صلاحية بعض الفلزات الثقيلة للنبات فى الاراضى الملوثة بإستخدام كمبوست قش الارز وبقايا محطة معالجة المياه

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أجريت دراسة تأثير الكمبوست المصنع من قش الارز وبقايا محطة معالجة المياه على تثبيت الفلزات الثقيلة فى الارض الملوثة ونمو نبات الكانولا. لذلك أخذت عينات سطحية مركبة من الاراضى الزراعية بمنطقة المحله الكبرى، محافظة الغربية للدراسة. هذه الاراضى على مر عشر سنوات كانت تروى بمياه صرف تستقبل مياه صرف صحى وصناعى بدون معالجة من مصانع منطقة المحله الكبرى. أوضحت النتائج انخفاض معنوى فى تركيز الرصاص والكادميوم والزنك لجذور وسيقان نبات الكانولا وكذلك الكمية المستخلصة من الارض لهذه العناصر باضافة كمبوست قش الارز وبقايا محطة معالجة المياه مقارنتا بالكنترول(الارض الملوثة). كما زاد الوزن الجاف لنبات الكانولا زيادة معنويا مع اضافة كمبوست قش الارز وبقايا محطة معالجة المياه بمعدل ٢٠،١٠ جم/كجم ارض بالمقارنة مع الكنترول. وأعطيت المعاملة كمبوست قش الارز عند خلطها مع بقايا محطة معالجة المياه بنسبة ٢:١ او ١:١ كوزن أعلى وزن جاف لنبات الكانولا وايضا انخفاض تركيز الفلزات الثقيلة فى جذور وسيقان نبات الكانولا مقارنتا بالمعاملات الاخرى. وهكذا يعتبر خلط الكمبوست المصنع من قش الارز مع بقايا محطة معالجة المياه ذو كفاءة فى أنخفاض صلاحية وزيادة قدرة الارض على تثبيت الفلزات الثقيلة فى الارض وزيادة محصول الكانولا وايضا تحسين كفاءة اعادة الاستخدام او التخلص من قش الارز وبقايا محطة معالجة المياه لما لهما من خطورة على البيئة والانسان.