

**IMPACT OF Fe/Mn-MODIFIED DRINKING WATER  
TREATMENT RESIDUALS ON HEAVY METALS  
IMMOBILIZATION IN SEWAGE SLUDGE  
CONTAMINATED soil**

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**ABSTRACT**

Recently, drinking water treatment residuals (Al-WTRs) received great attention as a low-cost immobilizing agent for heavy metals in contaminated soil in order to improve its immobilization efficiency. Al-WTR modified using some active sorbents, as Fe-Mn oxides, in this work, Al-WTR modified using  $\text{Fe Cl}_2 \cdot 4\text{H}_2\text{O}$  combined with  $\text{KMnO}_4$  and we examined the impact of raw and Fe/Mn- modified Al-WTR at different rates (0, 0.5, 1.5, and 2.5%) on the chemical behavior of Zn, Cr, Cd and Pb through fractionation trial after two months of incubation. In addition, investigated bioavailability of these metals in soil through pot experiment using radish plant (*Raphane's sativus*) as a bio-indicator. The results showed that Fe/Mn- modified Al-WTRs has greater effect on redistribution of heavy metals among their fractions where the exchangeable, and carbonate fractions significantly decreased. However, the oxides-, organic-bound and residual fractions increased significantly ( $P < 0.05$ ) in the soil for all elements relative to raw Al-WTRs and untreated soil. As well, bioavailability of Zn, Cr, Cd and Pb decreased with increasing raw and Fe/Mn- Al-WTR rate. 2.5% Fe/Mn- modified Al-WTR was significantly more effective in reducing the concentrations of DTPA-Zn (up to 73.3%), -Cr (up to 65.2%), -Cd (up to 73.6%) and -Pb (up to 90.7%) in the soil. The results also demonstrated that these heavy metals concentrations in shoot and root decreased with increasing Fe/Mn- Al-WTR dosage., 2.5% Fe/Mn- modified Al-WTR decrease the percentage of Zn, Cr, Cd, and Pb in shoot by 48.46, 66.24, 68.75 and 81.55% respectively. It can be suggested that modification of the raw Al-WTR increased its specific surface area, active functional groups (Fe-O and Mn-O) and CEC, which led to increasing its immobilization efficiency and played an important role in stabilization of heavy metals in the forms of oxides, organic and residual fractions.

**Key Words:** Al-WTR, Fe/Mn-modified Al-WTR, heavy metals, fractionation, immobilization

## INTRODUCTION

Soil contamination with heavy metals has rapidly increased and become a global concern during the last few decades **Yang et al., (2018)**. The excessive and permanent presence of heavy metals in a soil that caused by anthropogenic activities, has harmful potential hazards to groundwater, agricultural productivity, and particularly to human health. One of the amiable in situ remediation approaches for heavy metals contaminated soils remediation is the in-situ immobilization technique. In-situ metal immobilization is a simple, cheap, and environmentally friendly approach via using soil amendments for reducing the metals bioavailability and mobility by sorption, complexation, and/or co-precipitation (**Palansooriya et al., 2020**). During drinking water treatment, many low-cost coagulating and flocculating agents as alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ], are often applied for the precipitation of undesired suspended solids and water purification **Lombi et al., (2010)**. Al-WTR is generated in the process of cleaning potable water. On a global scale, several million tons of WTR sludges are produced every year (**Ahmad et al. , 2016**). Therefore, WTRs sludge needs applicable and low-cost approaches for sustainable management. One of these approaches is using these wastes as an immobilizing agent for treating of heavy metals contaminated soils and water (**Shen et al., 2019a**). Due to specific characteristics of WTR, such as its high porosity, amorphous phases and the presence of Fe and Al (hydr) oxides makes it has high potentiality usage as a sorbent for bio-and chemical- pollutants in water and as soil amendment (**Xu et al., 2019**). Nevertheless, the Al-WTR application reduced heavy metals mobility and bioavailability in soils (**Shaheen et al., 2017**). Raw waste materials as WTRs often have relatively low immobilization efficiency. Therefore, chemical modifications might be applied in order to enhance their immobilization efficiency. Recently **Ibrahim et al. (2020)** have reported that Fe-Mn oxides and phosphates could be used as efficient sorbents/immobilizing agents for heavy metals stabilization in water and soils. However, these oxides due to their small-scale size may be apt to agglomeration, which reduces their direct usage as adsorbents (**Tyson et al., 2011**). **Xu et al., 2019, (2020)**, studied the potential of metal-modified WTRs to remove phosphorus and the pathogens from storm water. However, the effectiveness and suitability of modified-WTR as an immobilizing agent for remediating heavy metals contaminated soils is not sufficiently assessed. The current work was aimed to investigate the effect of raw and Fe/Mn modified Al-WTR on the redistribution of Zn, Cr, Cd and Pb among their fractions in contaminated soils and assesses their efficiency as immobilizing agents for remediation heavy metals contaminated soils

## MATERIALS AND METHODS

### Sampling and characterization of soil and Al-WTR

A composite surface layer (0-30 cm.) of soil sample was collected from Al-Gabal Al-Asfar area, Qalyubia Egypt, which was contaminated with heavy metals either because of sewage sludge or effluent applications. The soil sample from Al-Gabal Al-Asfar farm (30°13' N 31°23' E), which is being used to dispose sewage sludge and effluents from the Wastewater Treatment Plant for Cairo Metropolitan for more than 70 years. Alum-Water treatment residuals (Al-WTRs) were collected from water treatment plant, where Alum [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O] is used, El-Marg water station, Cairo, Egypt. Collected soil and Al-WTR samples were air-dried, ground, and then passed through a 0.2mm sieve and characterized. Mechanical analysis of soil texture was carried out by using international pipette method **Syvitski (2007)**. Soil pH and electrical conductivity (EC) were measured in soil suspension (1:2.5 w/v) (**Black, 1965**). Cation exchange capacity (CEC) was determined using sodium acetate method (**Rhoades, 1982**). Soil organic carbon (SOC) was determined by Walkley-Black method (**Black, 1965**). Total carbonate content was determined using Collin's calcimeter. DTPA-extractable of heavy metals was determined using an ammonium bicarbonate-DTPA according to **Barbarick and Workman (1987)** in soil & Al-WTR and measured by ICP (Inductively coupled plasma-mass spectrometry). Total heavy metals were determined by the method described by **Ure (1995)** and measured by ICP Preparation of the Fe/Mn modified Al-WTR (Fe/Mn-Al-WTR). The Fe/Mn modified Al-WTR (Fe/Mn-Al-WTR) was obtained according to the method of **Jiang et al., (2018)**, through the raw Al-WTRs was treated with FeCl<sub>2</sub>·4H<sub>2</sub>O in the presence of KMnO<sub>4</sub>. Five grams of Al-WTR were added into 25 mL of 0.21 mol L<sup>-1</sup> KMnO<sub>4</sub> solution and stirred for 2 h, then adding 25 mL of 0.49 mol L<sup>-1</sup> FeCl<sub>2</sub>·4H<sub>2</sub>O solution and continually stirred for 2 h subsequently, adjust the pH of the solution at 6-7 by 1 mol L<sup>-1</sup> Na OH and shaken continuously in a water bath at a temperature of 40 °C. After 2 h the reaction was completed, the Fe/Mn modified Al-WTR was taken out and allowed to stand for 24 h. The modified Al-WTR was rinsed with distilled water several times to neutrality and oven dried at 105 °C.

### Characterization of Al-WTR and Fe/Mn modified Al-WTR

The specific surface area of the two amendments (Al-WTR and Fe/Mn-Al-WTR) was measured by BET/N<sub>2</sub>-adsorption method (**Zhou and Haynes, 2011**). The crystallographic structures of Al-WTRs and Fe/Mn- modified Al-WTRs surface were assessed by powder (less than 2 μ) X-ray diffraction (XRD). Identification of different clay and non- clay minerals was carried out following the criteria established by **Moore and Reynolds (1989)**. In addition, the active functional groups of Al-WTR and Fe/Mn- modified Al-WTR were characterized by ATR-FTIR FTIR spectrometer Spectroscopy, THERMO NICLOT, 50. with a mid-IR measurement in region of 4000–400 cm.<sup>-1</sup> (**Michal et al., 2011**).

The surface and structural morphology of the Al-WTRs and Fe/Mn-Al-WTRs were characterized by using high resolution Scanning Electron Microscopy (SEM). Analysis experiments were carried out on a FEI Quanta FEG 250 instrument. EDX, is an X-ray technique used to identify the elemental composition of materials. EDX systems are attachments to (Scanning Electron Microscopy (SEM) instrument where the imaging capability of the microscope identifies the specimen of the Al-WTRs and Fe/Mn-Al-WTRs.

#### **Pot experiment**

To assess the suitability and effectiveness of Al-WTR and Fe/Mn modified Al-WTR as immobilizing agents for heavy metals a pot experiment was carried out in plastic pots in the green house of the Soil Chemistry and Physics Department Desert Research Center Cairo-Egypt. The experiment was set up in a completely randomized block design with three replicates. Plastic pots containing 2.5 kg of sandy loam soil were thoroughly mixed with the recommended rates of N, P and K. The Al-WTR and Fe/Mn-Al-WTR were added to the soils at the rate of 0, 0.5, 1.5, and 2.5% w/w. Plastic bags were used inside the pots to avoid metals leaching out of the pots during the experiment course. Each pot was irrigated with tap water at 70% of maximum water holding capacity. The treatments were incubated at the laboratory conditions ( $23\text{ }^{\circ}\text{C}\pm 2$ ) for 60 days. After incubation period, the soil in each treatment was taken out and mixed thoroughly to obtain a homogenized sample from each pot, and 40 g soil was taken, air-dried and ground for further investigation. The homogenized soil samples were put in the pots again and radish plant (*Raphanus sativus*) was used as a bio indicator for environmental pollution (Hassan *et al.*, 2018). Where 5 seeds/pot were sown on 6/10/2023 then foliated to 2 plants per pot, The moisture content of soil in each pot was adjusted to 70% of water holding capacity of soil by compensating the loss in weight with tap water on every alternate day and radish plants were collected at preflowering time, i.e., after 40-45 days.

#### **Plant analysis**

After plant harvest and the roots were separated from the aerial parts, the radish samples (roots and shoots) were thoroughly washed and dried at  $70^{\circ}\text{C}$ . Fresh and dry weights were recorded, and plant samples were wet-digested by  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ , (Nicholson, 1984). Then Zn, Cr, Cd, and Pb were measured by ICP (Inductively coupled plasma-mass spectrometry).

#### **Fractionation of heavy metals**

The sequential extract method (Tessier *et al.*, 1979) was used to determine the speciation of heavy metals in control and treated soils. Where metals were fractionated for the exchangeable (Exch.) (1 M  $\text{MgCl}_2$ ), the carbonates-bound (Carb.) (1 M  $\text{NaOAc-HOAc}$ ), the oxides-bound (Oxid.)

(1M NH<sub>2</sub>OH-HCl in 25%(v/v) HOAc) and the organic-bound (Org.) fractions (0.02 M HNO<sub>3</sub>+30% H<sub>2</sub>O<sub>2</sub>NH<sub>4</sub>OAC in 20% HNO<sub>3</sub>). The residual fraction (Res.) was obtained as subtraction sum of fractions from the total content of heavy metals as follows: residual = total metal content – (Exch. +Carb. + Oxid. + Org.).

### Statistical Analysis

The significance test was carried out using ANOVA test. The least significant difference test (L.S.D) at 0.05 and 0.01 levels of probability according to **Steel et al. (1997)**. In addition to Pearson's correlation coefficient, were applied for a better understanding of the relationship among the measurements of the soils and effect of the treatments using IBM SPSS Statistics 20

## RESULTS AND DISCUSSION

### Characterization of studied soil and amendments

Results in Table 1a show that the soil texture of Al-Gabal Al-Asfar soil was sandy loam, as coarse and fine sand constitute 71.11%, as shown in the Table 1b. The studied soil was slightly alkaline (pH 7.92). As for the total dissolved salts, (EC dS/m) the soil of Al-Gabal Al-Asfar was saline (4.10 dS/m). Poor in OM (21.65 gkg<sup>-1</sup>) and had low cation exchange capacity (CEC; 9.52 cmolckg<sup>-1</sup>). The results showed that the total content of calcium carbonate (CaCO<sub>3</sub>) was 26.62gkg<sup>-1</sup>. Therefore, the soil was classified as non-calcareous. Chemically extractable Zn, Cr, Cd, and Pb concentrations of the soil were 88.47, 17.85, 2.96 and 16.72 mgkg<sup>-1</sup> respectively. The total Cd, Cr, Pb and Zn concentrations of the soil were 13.16, 116.32, 106.95 and 451.38mgkg<sup>-1</sup>, respectively. These values are higher than the limits of maximum permissible levels of total metals (mgkg<sup>-1</sup>) of **Kabate-Pendias and Pendias (2001)** [Pb (100 mg kg<sup>-1</sup>), Cd (5 mg kg<sup>-1</sup>), Cr (100 mg kg<sup>-1</sup>) and Zn (300 mgkg<sup>-1</sup>)]. The Al-WTRs was slightly alkaline (pH = 7.33), with higher CEC (42.91 Cmolckg<sup>-1</sup>) and contain higher OM (49.95 g kg<sup>-1</sup>) than the soil and low total content of calcium carbonate (CaCO<sub>3</sub>) was 18.9 gkg<sup>-1</sup>. As for the total dissolved salts, (ECdS/m) the Al-WTR was non-saline (0.93 dS/m). The Al-WTR was dominated by Aluminum (38.93 g kg<sup>-1</sup>), but it contained low Fe (6.45gkg<sup>-1</sup>).

**Table 1a: Some physical properties of the experimental soil**

location	C.S %	F.S %	Silt %	Clay %	Textural class	Field capacity (%)	Wilting point (%)	Available water (%)
Al-Jabal Al-Asfar	20.29	50.82	15.38	13.51	Sandy loam	17.38	7.55	9.83

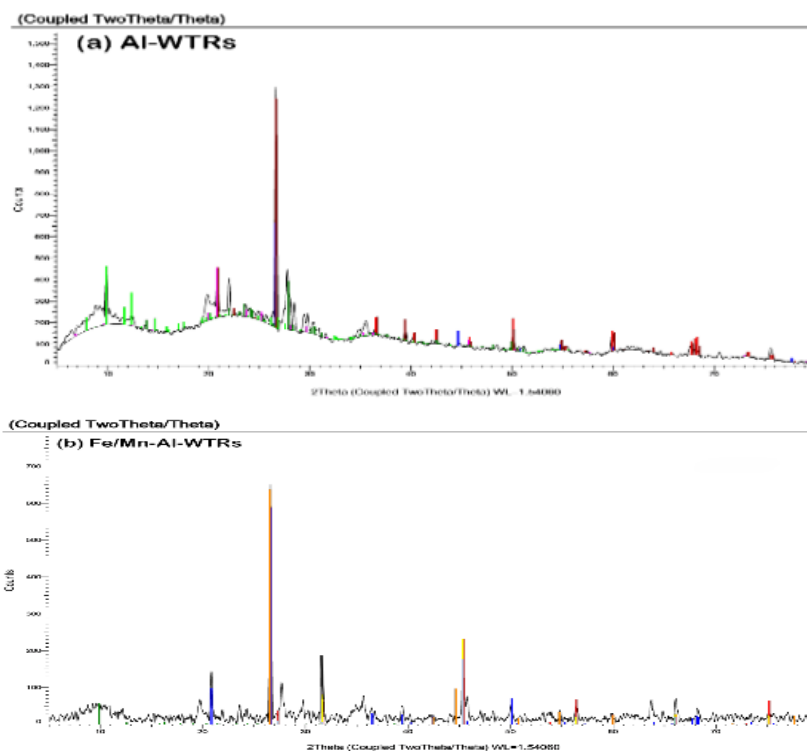
\*Not. C.S= Coarse sand and F.S =Fine sand

**Table 1b: Some chemical properties of the experimental soil and water treatment residuals (WTRs)**

Parameter	Al-Gabal Al-Asfar soil	Al-WTRs
pH (1:2.5)	7.92	7.33
EC dS/m(1:2.5)	4.10	0.93
Organic matter (gkg <sup>-1</sup> )	21.65	49.95
CaCO <sub>3</sub> (gkg <sup>-1</sup> )	26.62	18.90
CEC (cmol.kg <sup>-1</sup> )	9.52	42.91
Total Al(gkg <sup>-1</sup> )	21.6	38.93
Total Fe(gkg <sup>-1</sup> )	8.36	6.45
Total content of studied heavy metals mgkg <sup>-1</sup>		
Zn	451.38	11.92
Cd	13.16	ND
Cr	116.32	61.30
Pb	106.95	2.89
DTPA extractable heavy metals mg.kg <sup>-1</sup>		
Zn	88.47	0.23
Cd	2.96	ND
Cr	17.85	1.04
Pb	16.72	0.85

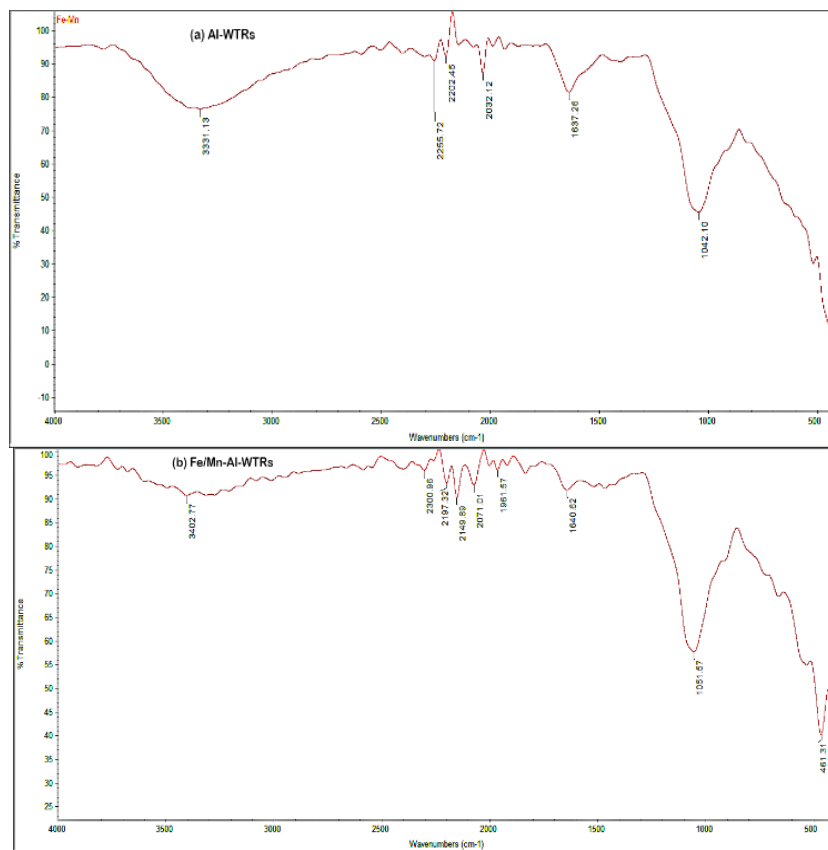
### Structural characterization of raw and Fe/Mn modified Al-WTRs

The specific surface areas (SSA) of two amendments were 9.48 and 96.65 m<sup>2</sup>g<sup>-1</sup> for Al-WTR and Fe/Mn-Al-WTRs, respectively. The Fe/Mn modification of Al-WTRs increased its porosity and increased its specific surface area by 10.2 folds indicating that modification of Al-WTRs using FeCl<sub>2</sub>·4H<sub>2</sub>O combined with KMnO<sub>4</sub> increased the SSA which may increase the ability of modified Al-WTR for immobilization of heavy metals. These results are in agreement with findings by **Elkhatib and Moharem (2015)**. Fig. 1 showed that XRD patterns of the raw and modified Al-WTRs materials which obtained from the X-ray diffraction analysis. The Al-WTRs material contained quartz (SiO<sub>2</sub>) and Kaolinite-Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (OH)<sub>4</sub> as well as mineral epistilbite CaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>·5H<sub>2</sub>O, the main crystalline components in the raw Al-WTR. Interestingly, Fig 1a also showed fund that the raw Al-WTRs was highly crystalline and had a high intensity diffraction peak between 25°-30° for silicon dioxide while for the Fe/Mn-Al-WTRs no obvious diffraction patterns were shown resulting from Fe/Mn species in the XRD patterns which is probably related to the amorphous nature of Fe/Mn. These amorphous forms reflected in increasing the specific surface areas and were useful for adsorption capacity as was found by **Wang et al. (2011)**. The modified Al-WTRs sample clearly had silicon dioxide, but these diffractions are significantly weakened. Also, the epistilbite diffraction is significantly weaker relative to raw Al-WTR.



**Fig. 1.** XRD spectra of (a) Al-WTRs and (b) Fe/Mn-Al-WTRs

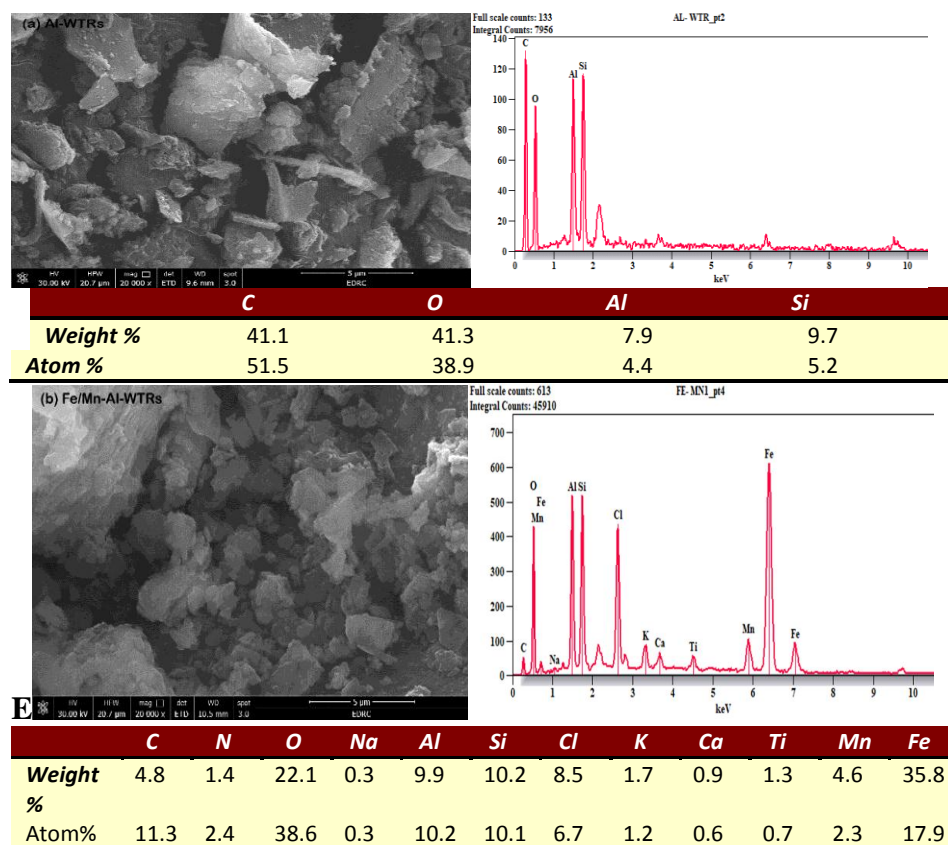
In Fig. 2a, the FTIR spectrum of raw Al-WTRs, the absorption bands occurred at  $3620$  and  $3421\text{ cm}^{-1}$  are resulting from the stretching OH groups. Absorption at  $3331\text{ cm}^{-1}$  is related to the OH stretching vibrations of  $\text{H}_2\text{O}$  in WTRs and in KBr. In IR spectrum it is also possible to observe the most significant band of the stretching vibration of Si-O at  $1061\text{ cm}^{-1}$ . Absorption bands in the range  $800\text{--}700\text{ cm}^{-1}$  are for Si-O stretching of silica and quartz. The bending vibration bands at  $527$  and  $468\text{ cm}^{-1}$  are related to Si-O-Al and Si-O-Si, respectively ( **Slaný *et al.*, 2019**). The modification of Al-WTRs by Fe/Mn ions resulted in new bands formation as well as changing intensities in the infrared spectra. The appearance of well-defined absorption band at  $574\text{ cm}^{-1}$  is due to the presence of iron–oxygen **Carabante *et al.*, (2009)**. The IR band of manganese oxide is observed at  $461\text{ cm}^{-1}$  **Kang *et al.*, (2007)**. By infrared spectroscopy we observed the increase in hydrophilicity of the modified samples and increase the intensity of the absorption bands of the OH groups of water.



**Fig. 2.** FTIR spectra of Al-WTRs (a) and Fe/Mn-Al-WTRs(b).

The SEM-EDX is an effective analysis to describe surface morphology and elemental composition in micro-scale of studied samples (Li *et al.*, 2019). The SEM image of the Al-WTRs (Fig. 3a) shows that Al-WTRs exhibit a smoothly layered structure with both large and small particles in slice shape with sharp edges and corners. While the modified Al-WTRs contain loose and coarse in surface structure without sharp edges and corners (Fig. 3b). The Fe/Mn-Al-WTR has more pores than the Al-WTRs, with a lot of small particles attached to the surface (Fig. 3b), which confirm that the Fe/Mn-Al-WTRs has a higher surface area than the raw Al-WTR sand. The SEM-EDX spectra indicated that the Fe/Mn-Al-WTRs showed stronger Fe and Mn signals than the raw Al-WTRs, which confirm that the Fe/Mn-Al-WTRs contains Fe/Mn oxides. All these results confirm the potentially high sorption/immobilization efficiency of the Fe/Mn-Al-WTRs as compared to the raw Al-WTRs.

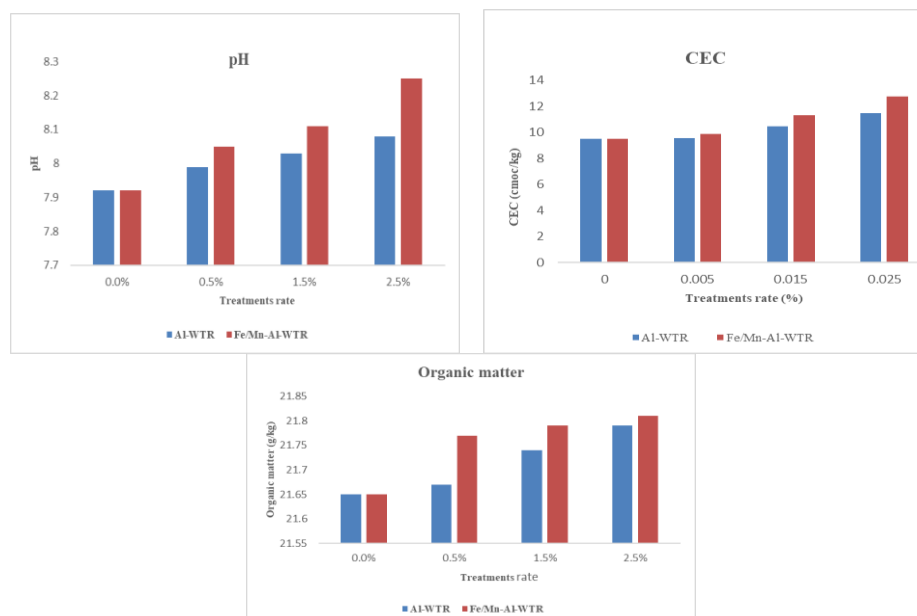




**Fig. 3.** The SEM images and SEM-EDX spectra of Al-WTRs (a) and Fe/Mn-Al-WTRs (b).

### Effect of the raw and modified Al-WTRs on soil properties

All treatments increased significantly soil pH (Fig. 3a). The highest pH value (8.25) was observed in the 2.5% Fe/Mn-Al-WTRs treatment. All treatments at the rates 1.5 and 2.5% increased significantly soil CEC from  $9.52 \text{ cmol}_c\text{kg}^{-1}$  in the control soil to  $11.33$  and  $12.75 \text{ cmol}_c\text{kg}^{-1}$  in the Fe/Mn-Al-WTR treated soil (Fig. 3b). Soil CEC increased by 20.5% and 33.9%, with Al-WTRs and Fe/Mn-Al-WTRs as compared to the control. The highest CEC values observed in the WTRs treated soil is attributed to Al-WTRs high CEC itself (Table 1b). Soil amendments, particularly the higher doses of the Al-WTRs, increased significantly soil OM (Fig. 3c). These results indicate that the application of Al-WTRs can improve soil OM, which is attributed to the substantial amount of OM contained in the WTRs, as also reported by *Dassanayake et al. (2015)*.



**Fig. 4.** Impact of Al-WTRs and Fe/Mn-Al-WTRs, on soil pH (a), CEC (b) and OM (c).

### Effect of raw and Fe/Mn modified Al-WTRs application on heavy metals fractions in soil

The mobility of the metals considering their abundance in the fractions take the order: exchangeable > bound to carbonate > bound to oxides > bound to organics > residuals (Tessier *et al.*, 1979). The exchangeable and bond to carbonates species are generally called bio-available. Oxides exist as nodules and cement between particles. These oxides bind trace metals can be mobilized under reducing and acidic conditions. The bond to organic species is relatively stable in nature and unavailable but can be mobilized under strong oxidizing conditions due to organic matter degradation (Haung *et al.*, 2007). In the untreated soil the distribution of Zn, Cr and Pb among their fractions was as follow Resi. >Oxide > Org. >Carb. > Exch. However, for Cd was as follow Resi. > Org. > Oxide > Carb. > Exch where the residual fraction is the predominant fraction in the control for all studied metals followed by oxides-bound fraction in soil. However, after treatment, the percentage of Fe-Mn oxides-bound and organic fractions increased in the soil for all elements followed by residual fraction.

#### Zinc

The distribution of Zn among its fractions before treatments application was as follow: Oxide (21.5%) > Org. (17.6%) > Carb. (14.1%) >Exch. (5.5%),

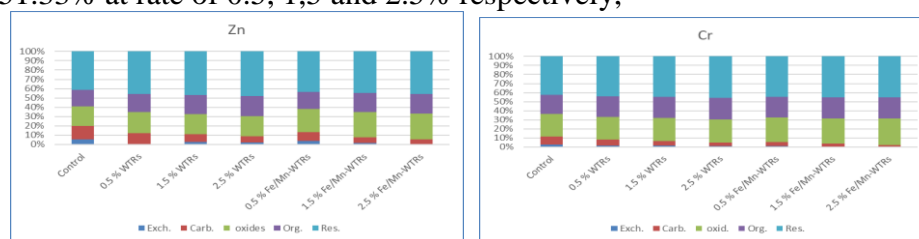
where the residual fraction made about 41.3% of the total Zn in the untreated soil. The highest content of the Oxide-Zn is possibly due to the presence of SOM content as suggested by **Chahal *et al.*, (2005)** who reported a significant positive correlation between Oxide Zn and organic carbon content in soils. It is clearly that in comparison with the untreated soil, the raw and modified Al-WTRs additions increase the Org, Oxide-Zn and residual fractions over the incubation period together with a gradual decrease in the Exch. and Carb-Zn fractions. Figure (4) illustrates the changes in zinc fractions as results of treatment application to the studied soil. Exch- and Carb-Zn decreased by increasing treatments dosage. Al-WTRs addition at 0.5, 1.5 and 2.5% decreased significantly Exch. - Zn at ( $p < 0.05$ ) by 24.85, 47.44 and 63.15 % respectively compared to the control. And also decrease Carb-Zn by 17.27, 41.78 and 52.01% respectively. Meanwhile Fe/Mn-Al-WTRs was more effective in decreasing the Exch. and Carb- Zn fractions where the Exch.- Zn decreased significantly at  $P < 0.05$  by 36.57, 71.61 and 87.31% and also reduced Carb-Zn by 31.57, 54.98 and 67.71% at rates of 0.5, 1.5 and 2.5% respectively, However, Al-WTR application to the studied soil led to increase in the org-Zn and residual fractions where the org-Zn increased by 6.61, 13.57 and 21.63% and the residual by 6.08, 14.21 and 16.23% at rates of 0.5, 1.5 and 2.5%, respectively. While Fe/Mn-Al-WTRs led to higher increments in Oxide-Zn, where increased by 31.57, 54.98 and 67.71% at rates of 0.5, 1.5 and 2.5%, respectively, followed by increasing in org-Zn and residual fractions from 17.6 to 22.86, 34.73 and 37.50% and from 41.3 to 46.58, 48.78 and 52.54% at rates of 0.5, 1.5 and 2.5%, respectively.

### Chromium

As shown in Fig.4, the distribution of Cr, among its fractions, before treatments application was: Oxide (24.76%) > Org. (21.02%) > Carb. (9.11%) > Exch. (2.47 %). Chromium is mostly abundant in residual fraction. The abundance of Cr in residual fraction was 48.98  $\text{mg kg}^{-1}$  soil which constitute 42.04% of soil total Cr. Results shown in Fig.4 illustrate that addition of amendments had great influence on Cr redistribution. Where with the increase of amendments (Al-WTRs and Fe/Mn-Al-WTRs) dose to the soil, both Exch. - and Carb- Cr proportions decreased sharply. Whereas the Oxid-, Org-Cr and the residual Cr proportions all significantly increased. With the application of Al-WTRs, the Exch.-and Carb-Cr prominently decreased by 36.81, 40.63 and 62.85% and by 27.52, 43.17 and 55.33% at rate of 0.5, 1.5 and 2.5% compared to control respectively indicating that 2.5% dose more effective in immobilizing Cr in the soil, moreover under applying Fe/Mn-Al-WTR the proportion of the Exch- and Carb-Cr decreased significantly at  $P < 0.05$  by 56.60, 72.92 and 78.13% and by 54.57, 64.66

and 80.02% at increasing dose (0.5, 1.5 and 2.5%) respectively. Fe/Mn-Al-WTRs were more effective in immobilizing available Cr in the soil.

On the contrary the oxide-bound Cr fraction increased significantly in the Fe/Mn-Al-WTRs treatment where increased by 10.40, 11.89 and 16.64% at rate of 0.5, 1, 5 and 2.5% respectively. No obvious difference was observed in the oxide-bound Cr in the Al-WTRs treatment, the Org-Cr and residual-bound Cr were both increased significantly at  $P < 0.05$  as compared to control. The percentage of Org-Cr as adding Al-WTRs increased from 21.02 % (control) to 29.31, 31.55 and 34.78% at rate of 0.5, 1.5 and 2.5% respectively. While with the application of Fe/Mn-Al-WTRs treatment the Org-Cr significantly  $< 0.05$  increased from 21.02 % (control) to 29.27, 31.47 and 32.75% at rate of 0.5, 1.5 and 2.5% respectively. Moreover the Al-WTRs treatment increased significantly the percentage of residual Cr from 42.04 % (control) to 46.82, 48.68 and 50.41 % at rate of 0.5, 1.5 and 2.5% respectively, and increased significantly  $P < 0.05$  with the application of Fe/Mn-Al-WTRs treatment from 42.04 % (control) to 47.94, 49.10 and 51.33% at rate of 0.5, 1.5 and 2.5% respectively,



**Fig.4.** Effect of raw and Fe/Mn-modified Al-WTR treatments on distribution of Zn and Cr among their fractions

### Cadmium

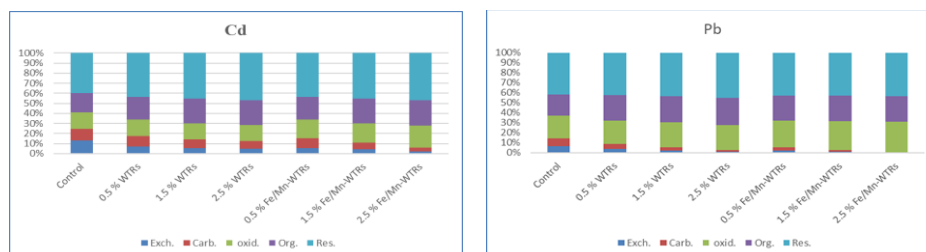
The distribution of Cd, among its fractions, before treatments application was: Org. (20.29%) > Oxide (16.79 %) > Carb. (11.55%) > Exch. (9.80 %) The residual fraction was 41.57% of soil total Cd. As can be seen from Fig. 5, the addition of raw and Fe/Mn modified Al-WTRs in the soil resulted to the Exch.-Cd significantly decrease by 31.04, 44.96 and 48.84 % (Al-WTRs) meanwhile decrease by 44.96, 58.91 and 80.62 % (Fe/Mn-Al-WTRs) at 0.5, 1.5 and 2.5 % dose, respectively. Moreover, the Carb-Cd decreased significantly by 7.89, 24.34 and 33.55 % (Al-WTRs) meanwhile decreasing by 15.14, 40.91 and 65.16 % (Fe/Mn-Al-WTRs) at 0.5, 1.5 and 2.5 % dose, respectively. No significant change was found in the oxide-bound Cd in the Al-WTRs treatment. While Fe/Mn-Al-WTRs treatment led to a significant increase in the oxide-Cd proportion where increased from

16.79% to 27.20, 30.36 and 40.36% at 0.5, 1.5 and 2.5 % dose, respectively. As shown in Fig. 5, the org-Cd increased by the same trend in both raw and Fe/Mn modified Al-WTRs treatments, where increased from 20.29 % (control) to 31.90, 40.89 and 54.36 % in 0.5, 1.5 and 2.5 % dose respectively. Proportion of residual Cd to the total Cd in soil increased significantly from 41.57.4 % (control) to 46.29, 50.71 and 54.37 % in the 0.5, 1.5 and 2.5 % Al-WTRs treatments, Fe/Mn-Al-WTRs. Residual Cd proportion increased significantly from 41.57.4 % (control) to 46.51, 51.08 and 56.74 % in 0.5, 1.5 and 2.5 % dose respectively. These indicated that more Cd in the soil was transformed from easily available to more stable Cd speciation.

### Lead

The distribution of Pb, among its fractions, before treatments application was: Oxide (22.42%) > Org. (20.67%) > Carb. (10.14%) > Exch. (6.35%). The residual fraction was 40.41% of soil total Pb as shown in Fig. 5. The Pb in the untreated soil was mostly classified as bound to Fe-Mn oxides and residual fraction. After the application of Al-WTRs and Fe/Mn-Al-WTRs, the Exch.-and Carb-Pb proportions decreased remarkably and even could not be detected in Fe/Mn-Al-WTR treatments when the dose was 2.5 % (Fig. 5). Where, the Exch- and Carb-Pb proportions decreased (Al-WTRs) by 42.27, 64.80 and 92.05% and by 52.66, 69.28 and 84.56% at rate of 0.5, 1.5 and 2.5% respectively. While the Exch- and Carb-Pb proportions decreased (Fe/Mn-Al-WTRs) by 66.27, 83.95 and 99.86 % and by 71.90, 85.15 and 99.94% at rate of 0.5, 1.5 and 2.5% respectively. Whereas the oxide-, org-Pb and the residual proportions were significantly increased, with increasing rates of amendments. Where with the application of Fe/Mn-Al-WTRs, the oxide- and org-Pb proportions significantly increased from 22.42 to 42.60, 49.98 and 66.76% and from 20.67% to 41.66, 45.27 and 45.73% at rate of 0.5, 1.5 and 2.5% respectively. When adding Al-WTRs, the oxide-Pb proportion insignificantly increased whereas org-Pb proportions significantly increased from 20.67 to 43.75, 49.89 and 54.65% at rate of 0.5, 1.5 and 2.5% respectively. While the application of Fe/Mn-Al-WTRs led to increase in the oxide- and org-Pb proportions where increased from 20.67% to 42.60, 49.98 and 66.76% and from 20.67 to 41.66, 45.27 and 48.73% at rate of 0.5, 1.5 and 2.5% respectively. These results indicated that the Fe/Mn-Al-WTRs treatment has greater effects in immobilizing Pb compared to WTRs and control.

Al-WTRs treatment and Fe/Mn-Al-WTRs treatments led to a significant increase in the residual Pb proportions where increased from 40.41 % (control) to 45.04, 48.65 and 52.90 % (Al-WTRs) at rate of 0.5, 1.5 and 2.5% respectively, and increased from 40.41 % (control) to 46.29, 54.25 and 56.52 % (Fe/Mn-Al-WTRs) at rate of 0.5, 1.5 and 2.5% respectively, It demonstrated that the application of Fe/Mn-Al-WTR had greater effects on the immobilization of Pb in contaminated soil.



**Fig.5.** Effect of raw and Fe/Mn-modified Al-WTR treatments on distribution of Cd and Pb among their fractions.

### Effect of raw and Fe/Mn modified Al-WTR application on DTPA-extractable heavy metals in soil.

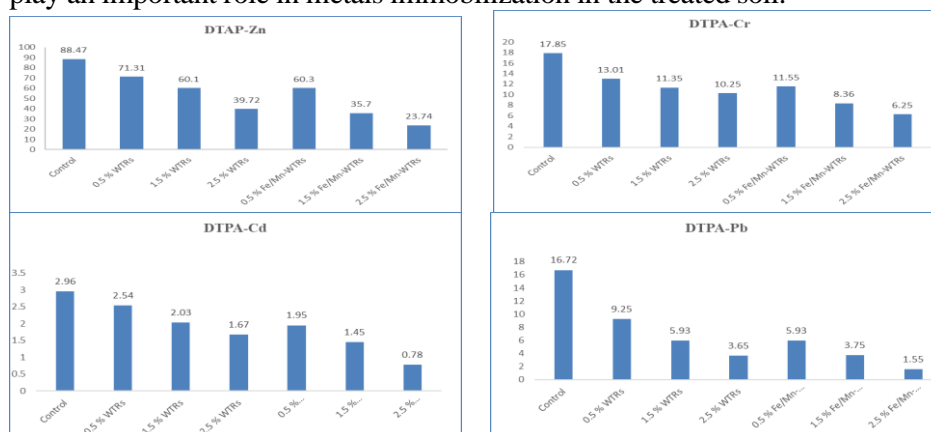
The DTPA-extractable metal species was used as an index for heavy metals bioavailability in soils. In comparison with the untreated soil, addition the raw and modified Al-DWRs decreased the availability of Zn, Cr, Cd and Pb. Fig.6 shows decrease in DTPA-extractable concentrations of Zn, Cr, Cd and Pb in soil according to different doses of raw and Fe/Mn modified Al-WTR compared to control. The results demonstrate that the metals availability decreased with addition of raw and Fe/Mn modified Al-WTR that can be related to the increase in soil pH, CEC, and OM which is expected to increase the sorption, complexation, and/or precipitation of these metals from the soil solution (**Shen *et al.*, 2019b**).

The decreasing in availability increased with increasing application rate of raw and Fe/Mn modified Al-WTR, which agree with the results presented by **Wang *et al.* (2021)** who studied the effect of different rates of raw and Fe/Mn modified Al-WTR on availability of Pb and Cu. As shown in Fig.6 after planting the decreases in DTPA- extractable of Zn, was higher in the 2.5% Fe/Mn modified Al-WTRs treatment, where decreased from 88.75 to 39.72 mgkg<sup>-1</sup> while in Al-WTRs decreased to 23.74mgkg<sup>-1</sup> where decreased by 55.2% (Fe/Mn-Al-WTRs) and 73.3% (Al-WTRs), relative to control which encourage increase residual fraction (precipitation) and decrease availability (**Zhou *et al.*, 2011**).

Also, the decrements in DTPA- extractable of Cr, were higher in the 2.5% Fe/Mn modified Al-WTRs than Al-WTRs treatment were decreased from 17.85 to 6.22 and to 10.25mgkg<sup>-1</sup>, where decreased by 42.6 and 65.2 % compared to control respectively. The available concentrations of Cd were reduced from 2.96 mg kg<sup>-1</sup> in the control soil to 1.67 and 0.78 mg kg<sup>-1</sup> in the 2.5% Al-WTRs and Fe/Mn-Al-WTRs treated soil respectively. Where decreased by Al-WTRs and Fe/Mn-Al-WTRs up to 43.6 and 73.6% compared to control. The available concentration of Pb was decreased from 16.72mgkg<sup>-1</sup>

in the control soil to 1.55 and 3.65 mgkg<sup>-1</sup> in the 2.5% Fe/Mn-Al-WTR and Al-WTR treated soil, the available concentrations of Pb decreased by 90.7% (Fe/Mn-Al-WTRs) and 78.2% (Al-WTRs), relative to Pb concentration in the untreated soil.

The Fe/Mn modified Al-WTR, showed higher ability for reducing the bioavailability of Zn, Cr, Cd and Pb than the raw material. This may be due to the modification of Al-WTRs which increased its porosity and increased its specific surface area. Therefore, the surface characteristics of raw and modified Al-WTR (e.g., functional groups) may explain the ability of these amendments to reduce metals bioavailability. The data of XRD indicated that Al-WTR contains mineral epistilbite and kaolinite these calcium aluminosilicate may play an important role in metals immobilization in the treated soil.



**Fig.6.** Effect of raw and Fe/Mn-modified Al-WTR treatments on DTPA-Zn, Cr, Cd and Pb in the studied soil after planting.

The FTIR spectra indicated that the raw and modified Al-WTR have active functional groups (e.g., -OH, Si-O-Si, and Si-O-Al), thus, larger sorption and immobilization of Zn, Cr, Cd and Pb by the modified Al-WTR might be related to the enrichment by these active surface groups as reported by **Li *et al.*, (2019)** and **Shen *et al.*, (2019a)**. The results also indicate that the modification of the Al-WTR increased the intensity of the absorption bands of the OH groups and also increased the hydrophilicity. These findings may confirm the successful modification of raw Al-WTR and explain the positive impact of Fe/Mn modification on increasing the sorption/immobilization efficacy of the Al-WTR for metals. Therefore, the Fe/Mn modification induced increase of Fe-Mn oxides content in the Fe/Mn-Al-WTRs may explain the higher immobilization efficacy by the modified Al-WTR than the raw material. In the modified Al-WTRs Fe/Mn oxides existed in amorphous form, which may enhance the

sorption/immobilization of metals. Fe/Mn oxides are generally characterized by an amphoteric nature, small particle size, high surface area with reactive surface sites, and low solubility under common soil pH values (**Bolan et al., 2014 and Scheinost, 2005**). These important properties keep them effective for immobilizing heavy metals through mechanisms such as co precipitation, specific sorption, and formation of inner-sphere complexes **Danila et al., (2020)**.

#### **Effect of raw and Fe/Mn modified Al-WTR treatments on radish plant content of heavy metals**

Results in Table 2, show that the studied heavy metals contents in radish roots were higher than that in the shoots compared to the untreated soil. The applied dosages of Fe/Mn-Al-WTR decreased Zn content significantly ( $P < 0.05$ ) in the shoots by 16.7-48.5% and by 7.1-31.5% with Al-WTRs. The Zn content in the roots was significantly reduced in the Fe/Mn-Al-WTR treatment by 31.1-74.9%, and in Al-WTR treatment by 23.8-56.1%, relative to the control. The concentrations of Cr in radish shoots decreased significantly ( $P < 0.05$ ) by 33.4-66.2% (Fe/Mn-Al-WTRs) and by 9.8-33.5% (Al-WTRs). However, the concentrations of Cr in radish roots decreased significantly by 27.5-68.4% (Fe/Mn-Al-WTR) and by 6.4-48.1% (Al-WTRs), compared to control.

The concentrations of Cd in radish shoots decreased significantly with the Al-WTR treatment by 1.8-30.9%. However, with the Fe/Mn-Al-WTR treatment by 24/6-68.8%. The concentrations of Cd in radish roots decreased significantly by 5.7-47.5% (Al-WTRs) and by 47.6-72.9% (Fe/Mn-Al-WTRs), compared to control. The applied dosages of Fe/Mn-Al-WTR decreased Pb content significantly ( $P < 0.05$ ) in the shoots by 33.5-81.5% while by 7.3-26.9% with Al-WTRs. The Pb content in the roots was significantly reduced in the Fe/Mn-Al-WTR treatment by 48.3-86.1% and in Al-WTR treatment by 5.4-25.8%, relative to the control. In general, increasing the treatments application dose decreased the studied heavy metals contents in radish roots and shoots. The significant reduction of Zn, Cr, Cd and Pb bioavailability and uptake in the treated soil is possibly due to the increase in soil pH, CEC, and OM which is expected to increase the sorption, complexation, and/or precipitation of these metals from the soil solution **Shen et al., 2019a and Wang et al., 2021**).

The results of Pearson correlation analysis (Table 3) confirm our explanation and indicated that the concentrations of DTPA- extractable metals were negatively correlated with soil pH ( $r = -0.949, -0.948; -0.985; P < 0.01$  for Zn, Cr and Cd respectively;  $r = -0.873; P < 0.05$  for Pb), with CEC ( $r = -0.939$  and  $-0.934; P < 0.01$  for Zn and Cd;  $r = -0.864$  and  $-0.788; P < 0.05$  for Cr and Pb). and with SOM ( $r = -0.934, -0.905, -0.936$  and  $-0.930; P < 0.01$  for Zn, Cr, Cd and Pb respectively). The concentrations of metals in the radish shoots were also negatively correlated with soil pH ( $r = -0.958, -0.882$  and -



.959;  $P < 0.01$  for Zn, Cr and Cd respectively;  $r = -0.844$ ;  $P < 0.05$  for Pb) and CEC ( $r = -0.964, -0.882, -0.925$  and  $-0.857$ ;  $P < 0.01$  for Zn, Cr, Cd and Pb respectively) and SOM ( $r = -0.917, -0.950$  and  $-0.882$ ;  $P < 0.01$  for Zn, Cr and Cd respectively;  $r = -0.828$ ;  $P < 0.05$  for Pb). These negative correlations may indicate that the decreasing of bioavailability of Zn, Cr, Cd and Pb associated by the increase in soil pH, CEC and SOM.

**Table 2. Effect raw and Fe/Mn modified Al-WTR treatments on radish plant (*Raphanus sativus*) heavy metals content**

treatment %	Heavy metals content in radish plant root (mgkg <sup>-1</sup> )				Heavy metals content in radish plant shoot (mgkg <sup>-1</sup> )			
	Zn	Cr	Cd	Pb	Zn	Cr	Cd	Pb
control	21.28a	11.85a	3.87a	7.25a	11.35a	7.85a	2.72a	5.69a
0.5%Al-WTRs	16.22b	11.05b	3.65b	6.86b	10.55b	7.08b	2.67ab	5.37ab
1.5%Al-WTRs	14.45c	8.75c	2.55c	6.02c	9.35c	5.65c	2.34b	5.07b
2.5%Al-WTRs	9.35d	6.15d	2.03d	5.38d	7.77d	5.21d	1.88c	4.23c
0.5% Fe/Mn-Al-WTRs	14.66c	8.59c	2.85a	3.75e	9.45c	5.23d	2.05bc	3.75d
1.5% Fe/Mn-Al-WTRs	8.36de	6.08d	2.01e	2.35f	7.03e	4.01e	1.33d	2.34e
2.5% Fe/Mn-Al-WTRs	5.34e	3.75e	1.05f	1.01g	5.85f	3.15f	0.85e	1.05f
Mean	12.81	8.03	2.57	4.66	8.76	5.31	1.98	3.93
LSD	0.05	0.01	0.01	0.11	0.02	0.03	0.01	0.01

The same letters in each column means that no significant difference presents at 0.05 level.

**Table 3. Pearson correlation coefficients between soil properties and metals content in soil and radish shoot**

Parameter	pH	CEC	O.M	Shoot-Zn	Shoot-Cr	Shoot-Cd	Shoot-Pb
Shoot-Zn	-0.958**	-0.963**	-0.917**	1			
Shoot-Cr	-0.882**	-0.882**	-0.950**	0.984**	1		
Shoot-Cd	-0.959**	-0.925**	-0.882**	0.972**	0.964**	1	
Shoot-Pb	-0.944**	-0.857*	-0.828*	0.922**	0.942**	0.984**	1
DTPA-Zn	-0.949**	-0.939**	-0.934**	0.991**	0.958**	0.942**	0.887**
DTPA-Cr	-0.948**	-0.864*	-0.905**	0.947**	0.962**	0.904**	0.876**
DTPA-Cd	-0.985**	-0.934**	-0.936**	0.981**	0.985**	0.964**	0.931**
DTPA-Pb	-0.873*	-0.788*	-0.930**	0.885**	0.914**	0.807**	0.760**

O.M: Organic matter; CEC: Cation exchange capacity. \* Correlation is significant at the level  $P < 0.05$ . \*\* Correlation is significant at the level  $P < 0.01$ .

## CONCLUSION

The modification of Al-WTRs using Fe/Mn increased its specific surface area, and increased the intensity of the absorption bands of the OH groups, as well as the hydrophilicity. In addition, modified samples still contained silicon dioxide and IR spectroscopy confirmed formation of new bands such as Fe-O and Mn-O. Also, the modification induced increase of Fe-Mn oxides content in the Fe/Mn-Al-WTRs on this material and increased soil pH, CEC and the presence of active functional groups (e.g., -OH, Si-O-Si, and Si-O-Al) may explain the higher immobilization efficacy by the modified Al-WTR than the raw material through redistribution of Zn, Cr, Cd and Pb fractions in soil. In this

study exchangeable and carbonate fractions for Zn, Cr, Cd and Pb significantly decreased with increase in Fe/Mn-Al-WTR, however fractions bound to oxides organic and residual fractions was increased. It was found that the raw and Fe/Mn- modified Al-WTR could immobilize Zn, Cr, Cd and Pb in the contaminated soil. It is clear that increasing Fe/Mn-Al-WTR rate significantly reduced the amount of DTPA-extracted metals in soil and thus, decreased their uptake by radish plant as compared to the untreated soil. However, the Fe/Mn-Al-WTR, were more effective in reducing the concentration of Zn, Cr, Cd and Pb in shoot and root in radish plant than the raw material. It could be concluded, that modification of Al-WTR using Fe/Mn increased its efficacy as soil amendment and immobilizing agent for heavy metals in soils and is considered environmentally friendly and low-cost trial for safe management of industrial waste.

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## تأثير مخلفات معالجة مياه الشرب المعدلة بالحديد / المنجنيز على تثبيت

### المعادن الثقيلة في التربة الملوثة بحمأة الصرف الصحي

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في الآونة الأخيرة، حظيت مخلفات معالجة مياه الشرب (AI-WTRs) باهتمام كبير كعامل تثبيت منخفض التكلفة للمعادن الثقيلة في التربة الملوثة، ومن أجل تحسين كفاءتها التثبيتية تم تعديل AI-WTR باستخدام بعض المواد الماصة النشطة مثل أكاسيد الحديد والمنجنيز. في هذا العمل تم تعديل مخلفات معالجة مياه الشرب (AI-WTR) باستخدام  $FeCl_2 \cdot 4H_2O$  مع  $KMnO_4$ .

ولهذا تم عمل تأثير AI-WTR الخام والمعدل بالحديد والمنجنيز بمعدلات مختلفة (0، 0.5 ، 1.5 ، 2.5%) على السلوك الكيميائي للعناصر الثقيلة المدروسة: الزنك - الكروم - الكاديوم - الرصاص من خلال تجربة التجزئة بعدالتحصين لمدة شهرين، وبالإضافة إلى ذلك

تم التحقق من التوافر الحيوي لهذه العناصر الثقيلة في التربة من خلال تجربة الأرصص باستخدام نبات الفجل (*Raphanus sativus*) كمؤشر حيوي.

أظهرت النتائج أن مخلفات معالجة مياه الشرب المعدلة بالحديد/المنجنيز لها تأثير أكبر على إعادة توزيع العناصر الثقيلة بين صورها حيث إنخفضت العناصر الثقيلة في الصورة المتبادلة والمرتبطة بالكربونات بشكل ملحوظ ، ومع ذلك، زادت الصور المرتبطة بالأكاسيد والمادة العضوية والمتبقية بشكل ملحوظ ( $P < 0.05$ ) في التربة لجميع العناصر الثقيلة بالمقارنة بمخلفات معالجة مياه الشرب الخام والتربة غير المعالجة.

كما أوضحت النتائج إنخفاض التوافر الحيوي لعناصر الزنك - الكروم - الكاديوم - الرصاص مع زيادة معدل مخلفات معالجة مياه الشرب الخام والمعدل بالحديد/المنجنيز . كما أظهرت النتائج أن إضافة 2.5% من مخلفات معالجة مياه الشرب المعدلة بالحديد/المنجنيز كان أكثر فعالية بشكل ملحوظ في تقليل تركيزات الزنك المستخلص بـ DTPA (حتى 73.3%) والكروم (حتى 65.2%) والكاديوم (حتى 73.6%) والرصاص (تصل إلى 90.7%) في التربة.

كما أوضحت النتائج أن تركيز العناصر الثقيلة في المجموع الجذري والخضري لنبات الفجل إنخفضت مع زيادة جرعة مخلفات معالجة مياه الشرب المعدلة بالحديد/المنجنيز وكانت إضافة 2.5% من مخلفات معالجة مياه الشرب المعدلة بالحديد/المنجنيز أدت إلى إنخفاض نسبة عناصر الزنك - الكروم - الكاديوم - الرصاص في المجموع الخضري بنسبة 48.46. و 66.24 و 68.75 و 81.55 % على التوالي.

وأكدت النتائج أن تعديل Al-WTR الخام أدى إلى زيادة مساحة سطحه المحددة والمجموعات الوظيفية النشطة (Fe-O و Mn-O) وسعته الكاتيونية التبادلية، مما أدى إلى زيادة كفاءته التثبيتية وله دوراً هاماً في تثبيت العناصر الثقيلة في الصور المرتبطة بالأكاسيد والمادة العضوية والمتبقية.