

Redistribution and Desorption Kinetics of Some Heavy Metals in Biosolids Treated Soils Amended with Water Treatment Residual Nanoparticles

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ABSTRACT

The study was designed to demonstrate the effect of water treatment residual nanoparticles amendments for 0.3% biosolids treated calcareous and sandy soils on Cu, Pb, and Ni fractions change and release during 60 days incubation period; included five wetting drying cycles regime. The redistribution of studied metals fractions for control soil (0%WTR) depended on soil and metal type. There was a pronounced decrease in metal-residual fraction at the end of the incubation period (60 days); while other fractions were occupied with these residual fraction- released metals. Application of nWTR to both soils substantially reduced the non-residual fractions (NORS) of Cu and Ni and simultaneously increased residual (RS) both metals fractions. Furthermore, both Pb-oxides and RS fractions were increased as a result of nWTR addition. The metals forms transformation for nWTR amended soils as the incubation time prolonged from 30 to 60 days was studied. The Cu-forms transformation remained relatively unaltered with slightly increase of RS Cu versus decrease of exchangeable and carbonate Cu. With respect to Pb and Ni, residual fraction was increased significantly and this increase was arisen from either the decrease of all fractions of Ni- NORS or Pb-organic fraction. The amount of desorbed Cu, Pb, and Ni from both soils using DTPA extraction was significantly decreased after application of nWTR within the five wetting drying cycles. All the kinetic data were well expressed using both intraparticle diffusion and Elovich models due to the high coefficient of determination (R^2) and low standard error (SE) values. The final results indicate the ability of nWTR to reduce heavy metals mobility in biosolid treated calcareous and sandy soils.

Key words: Biosolid, water treatment residual nanoparticles, incubation period, fractionation, desorption kinetic.

INTRODUCTION

The remarkable increase in global population and also the prompt outgrowth of industrial and agricultural activities led to solid wastes such as biosolids to increase rapidly (Shao et al. 2015). These biosolids are defined as heterogeneous substances of biological wastes produced from sewage treatment procedures that contains organic/ inorganic substances, bacteria, and colloid particles. Inappropriate disposal of biosolids such as incineration, land filling (Marguí et al., 2016; Kominko et al., 2017) and sea dumping can lead to several environmental troubles such as surface and

groundwater contamination, land degradation, and food chain contamination (Wong, 1995; Singh and Agrawal, 2008). From the environment point of view, agricultural land application of biosolids will be a best choice preference over the other disposal methods (Kacprzak et al. 2017); since it can produce significant benefits concerning soil fertility and plant growth (Herzel et al. 2015; Rigby et al. 2015; Grobelak et al. 2017). Although the high advantages of biosolids-agricultural application, the high content of certain heavy metals in biosolids may diminish its application (Turkdogan et al., 2003; Wang et al., 2003); since these metals may cause human health hazardous impact -via plant uptake- due to their accumulation in agricultural soils (McLaughlin et al. 2006; Wang et al. 2005). Therefore, the mobility and bioavailability of heavy metals (HMs) in biosolids amended soils should be minimized which can be properly achieved through well understanding the behavior of HMs under realistic conditions of contaminated soils.

Fate of heavy metals in soil environment are mainly depends on removal of metals from the soil solution towards solid surfaces (sorption), desorption of the metal from the soil particle to the soil solution, and precipitation-dissolution reactions of the metal (Sposito, 1989; Sparks, 2003). Furthermore, redistribution of metals among solid-phase components during different residence time can directly control metal mobility and toxicity in soils (Davies et al., 2003; Wu et al., 2006).

Furthermore, the physical, chemical, and biological processes occurring in irrigated soils could be strongly affected by the wetting-drying cycles (Han et al., 2001). This water periodic regime can simulate the real field irrigation in the semi-arid soils (Khodaverdiloos et al., 2012). It plays a vital function in governing the mobility of heavy metals and hence controls their possibility danger in contaminated soils. Furthermore, heavy metals redistribution and re-desorption could be affected (Zheng and Zhang, 2011; Yang et al., 2019).

The remediation technique of contaminants -such as HMs- that aims to decrease the concentration of dissolved contaminants by sorption and or precipitation knows as chemical immobilization (Basta and McGowen, 2004); which can be achieved by addition of organic/inorganic amendments to reduce contaminant

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solubility or bioavailability to the plants (Guo et al., 2006; Hashimoto et al., 2009). Using low cost waste materials as an immobilizing agents in HMs contaminated soils have been -recently- in growing interest (Bolan et al., 2014; Lu et al., 2017; Moharem et al., 2011 & 2016; Moharem, 2016). One of such materials is drinking water treatment residuals (DWTR). It is a waste that produces during drinking water treatment and contains aluminum salts for coagulation. DWTRs have a similar structure of noncrystalline aluminum hydroxide that behaves similar to amorphous Al soil mineral forms (Tisdale et al., 1985). These wastes have a multitude sorption surface sites due to their large surface area and microporous nature (Makris et al., 2004); consequently reuse of DWTR for sequestering heavy metals in contaminated soils has been newly condensed (Sarkar et al., 2007; Hovsepian & Bonzongo, 2009; Moharem et al., 2013; Moharem, 2012; Elkhatib & Moharem, 2015). Furthermore, increasing the sorption capacity of these wastes has been recently achieved by converting bulk DWTR to Nanoscale water treatment residual (nWTR) by precision milling (Elkhatib et al., 2015a). Despite of the successful proof of reusing nWTR in land application and wastewater (Moharem, et al., 2019; (Moharem, et al., 2019; Elkhatib et al., 2017, 2018, 2019), few studies regarding heavy metals stabilization in biosolid-added soils are revealed. Furthermore, information in the literature concerning kinetic release-modeling of HMs in nWTR-treated soils through different wetting-drying cycles is missing; since such information is critical in evaluating the expediency of nWTR as soil amendment. Therefore, this study aims to evaluate the effect of nWTR addition to Egyptian biosolids amended calcareous and sandy soils on : (1) redistribution of geochemical forms for Cu, Pb, and Ni after 12 days and 60 days incubation period, and (2) metals release-mathematically expressed- within five wetting (field capacity) drying cycles regime.

MATERIALS AND METHODS

Soils and water treatment residuals nanoparticles (nWTRs)

Two soil samples differed in texture and calcium carbonate content were utilized. Sandy soil (Typic Quartz zipsmments) was collected from Elbostan 80 Km south west Alexandria and calcareous soil (Typic Calciorthids) from El-Nahda 40 Km south west Alexandria. Soil samples were air-dried, passed through a 2-mm sieve and stored in plastic bags for later use. The drinking water treatment residuals (DWTRs) were collected from the Drinking Water Treatment Plant in Kafr El-Dawar, El-bahera governorate Egypt, and air-

dried prior to their use (Makris and Harris, 2005). Selected chemical and physical properties of soils and DWTRs are shown in Table 1. Soil electrical conductivity (EC) and pH were determined in the saturated soil paste extract and in 1: 2.5 suspension of DWTRs (Richards, 1954). The bioavailable Cu, Pb, and Ni were extracted by DTPA (Lindsay and Norvell, 1978) and measured by atomic absorption spectroscopy (contraAA 300). Soil organic matter content was estimated by the method of Walky and Black (Nelson & Sommers, 1982), total carbonate equivalent was determined by the calcimeter method (Nelson, 1982), and cation exchange capacity was measured by the method of Rhoades (1982). Particle size distribution analysis was determined by the hydrometer method (day, 1965). Total amount of Al in DWTRs was measured according to Ross and Wang (1993) method using acid ammonium oxalate.

Biosolids

The stabilized wastewater solids under controlled aerobic conditions that called biosolids were collected from Alexandria waste water treatment plant (N9). Table 1 illustrates chosen chemical properties of the biosolids. Aqua regia method were used for heavy metals total concentrations determination (Esakku, et., 2005; Shrivastava and Banerjee, 1998) by atomic absorption spectroscopy (contraAA 300). Total amount of organic matter were measured according to Walky and Black method (Nelson & Sommers, 1982).

Preparation of WTR nanoparticles (nWTR)

The nWTR were obtained from bulk WTR utilizing Fritsch planetary mono mill approach as described by Elkhatib et al. (2015a). The characteristics and element contents of nWTR were examined employing transmission electron microscopy, x-ray diffraction, scanning electron microscopy with energy dispersive X-ray (SEM-EDX; INCAX-Sight model 6587, Oxford Instruments, UK) and autosorb iQ surface area analyser (Quantachrome, USA), (Elkhatib et al., 2015b).

Incubation Experiment

Three nWTR rates (0, 0.1, 0.3%) and one rate of WTR (2 %, w/w) in addition to 3%, w/w biosolids were added to 1 kg/ soil, in the laboratory, to represent the field addition rates for DWTRs and biosolids. Soil samples were well mixed with biosolids and /or DWTRs. Hereafter, the mixture was incubated for 60 days in five wetting-drying cycles regime. Each cycle was continued for 12 days; the first 2 days was for adding water -at field capacity- while the 10 days rest was for air-drying. Each treatment was conducted in

Table1. Selected chemical and physical properties of the studied soils, DWTR, and biosolid

Characteristics	units	Calcareous	Sandy	DWTR	Biosolids
pH*		8.33±0.08	8.26±0.06	7.45±0.11	6.72±0.09
EC*	dS m ⁻¹	4.56±0.12	3.19±0.06	1.67±0.18	8.12±0.07
Clay	%	22.10±3.55	5.00±1.18	-	-
Silt	%	7.80±1.63	2.500±2.46	-	-
Sand	%	70.10±4.45	92.50±6.17	-	-
Texture		S C L	S	-	-
OM	%	1.5±0.67	0.4±0.06	5.70±1.25	492±2.87
CaCO ₃	%	22.4±0.79	3.6±0.18	3.48±0.19	-
CEC	cmol kg ⁻¹	15±0.41	6±0.69	34.78±2.06	-
Total Al	g kg ⁻¹	-	-	38.01±1.87	-
Total metal	mg kg ⁻¹				
Cu		0.198±0.12	0.218±0.22	2.87±0.13	385.93±5.65
Ni		0.159±0.09	0.393±0.14	4.63±0.23	26.83±1.34
Pb		0.905±0.11	0.712±0.13	3.06±0.12	219.24±4.87
Soluble Al	mg kg ⁻¹	-	-	1.80±0.14	-
DTPA-extractable metal	mg kg ⁻¹				
Cu		0.95±0.005	0.19±0.03	1.20±0.05	28.4±1.69
Ni		0.083±0.04	0.124±0.02	2.49±0.08	2.7±0.19
Pb		0.57±0.04	0.41±0.04	1.58±0.06	12.8±0.34
WHC	g kg ⁻¹	-	-	470.00±2.18	250±2.87

EC – electrical conductivity; OM – organic matter; CEC – cation exchange capacity;

WHC – water holding capacity; C – Clay; SCL – sandy clay loam; S – sandy;

pH* was measured in 1:2 H₂O extract; EC* was measured in soil paste

replicated pots. Subsamples were taken periodically after 15 days of each cycle for DTPA extraction; while subsamples were taken after the first (12 days) and the fifth (60 days) cycles for sequential extraction technique. In each cycle, soils through the first 2 days of incubation were wrapped to avoid evaporation, while the following 10 days the soils were permitted for air-drying at 25 °C. Before sampling, the soil was blended totally to maintain samples similarity.

DTPA and sequential extractions

The bioavailable form of heavy metals was determined in incubated soils using DTPA extraction according to Lindsay and Norvell, 1978 and measured by atomic absorption spectroscopy (contraAA 300).

Furthermore, sequential extraction technique was exercised to fractionate heavy metals in incubated soils that advanced by Tessier et al. (1979). Each heavy metal- fractions was operationally defined as follows: exchangeable fraction (extractable with 1.0M MgCl₂ at pH 7); carbonate bound fraction (extractable with 1.0M sodium acetate at pH 5); iron and manganese oxides fraction (extractable with hydroxylamine); organic matter fraction(extractable with H₂O₂ in 1M HNO₃); and residual fraction (difference between the total amount of metals in soil and the sum of the metals in the four fractions. All metals concentrations in the obtained

extracts were determined using atomic absorption spectroscopy (contraAA 300).

The fractionation technique supposed that metals linked with the residual fraction (RS) are more fixed, less labile and less available for plant uptake than metals linked with the non-residual fractions (NORS), the sum of all fractions except the residual fraction.

RESULTS AND DISCUSSIONS

Changes of metal fractions during incubation time

The redistribution of Cu, Pb, and Ni among different fractions of control studied soils amended with 0.3% biosolid after 12 days (1st cycle) and 60 days (5th cycle) was studied and the results are shown in Table 2.

Copper: After the 1st cycle the high percentage of Cu was observed in residual (47.82 %) or organic (32.67 %) fractions of calcareous or sandy soils, respectively. The high percentage of Cu in sandy soil-organic fraction could be explained by formation a very stable complexes with organic matter (Sancar et al., 2000; Zhou and Wong, 2001). In contrast, the least presence of Cu was found in exchangeable or carbonate fractions of calcareous or sandy soils, respectively. The low combination between Cu and carbonate fraction may be attributed to low calcium carbonate content in sandy soil (Table 1). Considerable changes in Cu fractions were noticed at the end of the incubation

period (60 days). As seen in Table 2, for both soils there was a marked decrease in Cu-residual fraction and this decrease was compensated with increasing of both Cu-oxide and organic fractions. Furthermore, the carbonate fraction of both soils was not significantly changed during 60 days incubation period since Cu can precipitate as CuCO_3 in the presence of calcium carbonate (Ponizovsky et al., 2007). The Cu-exchangeable bound fraction of sandy soil was increased over the 60 days incubation period; whereas this fraction in calcareous soil was not significantly changed.

The ability of heavy metals to be mobile in soil matrix could be mathematically expressed as the mobility index (MI) (Banat et al. 2003; Liu et al. 2007) which can be calculated according to the following model:

$$\text{MI} = \Sigma(\text{Fi}/\text{Ti})/n$$

Where F_i is the metal concentration in exchangeable fraction concentration of the metal, T_i is the total concentration of the metal, and n is the number of the soil samples. The high lability and bioavailability of heavy metals in soils could be expected with high value of MI (Ahumada et al. 1999; Narwal et al. 1999).

The mobility index of Cu was used to show the effect of incubation time on Cu mobility through both soils. The higher MI (%) of Cu in sandy soil (9.7) than calcareous soil (5.7) through 1st incubation period in addition to increasing Cu-MI in sandy soils up to 11.1 as a result of prolonging incubation time (60 days) indicates more availability and mobility of Cu in sandy soil than calcareous soil.

Lead: During the first 12 days incubation, Pb in calcareous soil was mainly associated with residual phase (44.5%) followed by carbonate phase (22.7%) while exchangeable phase displayed the least existence (3.2%). The high presence of Pb in carbonate fraction was compatible with the FTIR spectroscopy examination of Qian et al., 2017 who found Pb precipitate as hydrocerussite (lead hydroxycarbonate, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ or $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$). In sandy soils, Pb distribution among different phases was in the following order: oxide (35.1%) > residual (34%) > carbonate (14.5%) > organic (11.6%) > exchangeable (4.8%). The high ability of Pb to form both inner-sphere metal surface complexes and/or precipitate phases as metal hydroxide could be the reason for the high Pb percentage in oxide phase (Brown et al., 2001 and Sparks, 2001). The effect of 60 days aging on redistribution of Pb fractions was pronounced for both soils. As seen in Table 2, the exchangeable fractions of calcareous and sandy soils were significantly increased from 3.2% and 4.8% to 5.7% and 9.2%, respectively. In contrast, residual fractions of both soils were

dramatically decreased. Thus, Pb becomes increasingly available due to redistribution of Pb in exchangeable and residual fractions over 60 days incubation. However, the increase of Pb in oxide and organic fractions for both soils and carbonate fraction in calcareous soil over this period (Table 2) could recompense this Pb-available increase. Oxide fraction can be considered sinks for heavy metals in alkaline conditions (McBride, 1994); since several metals such as Pb can be adsorbed or diffused into the oxide structure, decreasing its mobility (Contin et al., 2008; Schwertmann and Taylor, 1989). Also, organic fraction can reduce Pb availability in highly pH value through formation of strong inner-sphere complexes between Pb and soil organic matter (Basta et al., 2005). Furthermore, metals mobility in carbonate calcium-rich soils could be significantly reduced (Elkhatib et al., 1991). The Pb mobility index in both soils increased as incubation time prolonged from 30 days to 60 days reflecting potential more Pb availability over incubation period.

Nickel: This metal showed the lowest changed among the studied metals- in metal redistribution over the incubation period. However, a lowering of the residual fraction for both soils and a conforming increase of Ni bound to oxides fraction was found (Table 2). The mobility index of Ni was also not significantly differed in both soils due to incubation time progress. The low Ni-fractions redistribution during incubation time is in line with Sánchez-Martín et al. (2007) study that discusses heavy metals fractionation -including Ni- of sewage sludge amended soils over 18 months incubation time.

With respect to all studied metals, in general, the decrease of residual fraction over 60 days incubation time was observed in both soils and simultaneously other fractions were occupied with these residual fraction- released metals. The redistribution of metals between residual and other fractions could be attributed to dissolution of sludge-inorganic and organic compounds existent in residual fraction causing meals concentration in other fractions to increase (Smith, 1996).

Effect of nWTR on metal fractions

The effect of 2% bulk WTR and 0.1% and 0.3% nWTR treated calcareous and sandy soils that amended with biosolid (3%, w/w) on Cu, Pb, and Ni fractionation was examined and the results are stated in Figure 1.

Application of both bulk WTR and nWTR treated both soils substantially reduced the NORS Cu/Ni fractions and simultaneously increased RS both metals fractions. At rate of 2% WTR, for instance, NORS-Cu and Ni fractions in sandy soil were decreased from 78.6% and 55.89% to 62.8% and 46% whereas RS-Cu

and Ni fractions were increased from 21.4% and 44.1% to 37.19% and 53%, respectively. Furthermore, addition of 2% WTR to both soils significantly increased both Pb-oxides and RS fractions since oxides and RS fractions of calcareous soil -as example- were increased from 15.9% and 44.5% to 19.5% and 47.6%, respectively. The increase of Pb associated with oxide fractions could also -in addition to RS fraction- contribute in Pb immobilization in soils since metal bound to oxide supposes to be less mobility and plant uptake availability (Phillips and Chapple 1995). These findings indicate the function of WTR in converting studied metals from the more labile form to more stable and less mobile form that coincide with preceding studies (Moharem, 2012; Moharem et al., 2013; Elkhatib and Moharem, 2015; Elkhatib et al., 2015). When nWTR at 0.3% rate was utilized, more existence of Cu, Pb and Ni were found in RS fraction up to 85.77%, 59.36%, and 88.18%, respectively with also less existence in NORS of Cu (14.23%) and Ni (11.82%) fractions regarding calcareous soil -as example. Furthermore, more Pb-oxide fraction of both soils was increased reaching 47.39% for sandy soil. These findings indicate the more nWTR effectiveness in reducing studied metals mobility in biosolid amended both soils which can be attributed to the large specific surface area and multiple active sites of nWTR than bulk one (Elkhatib et al., 2015b; Ponizovskii and Mironenko, 2001). These results are consistence with previous study concerning the potential of nWTR to immobilize heavy metals in contaminated soils (Moharem, et al., 2019; Elkhatib et al., 2018, 2017).

Effect of incubation time on metal fractions of nWTR-treated soils

The redistribution of Cu, Pb, and Ni forms after the 5th cycle (60 days) in studied soils as a result of adding 0.1% and 0.3% nWTRs was studied comparing with 1st cycle (12 days) and the results are illustrated in Table 2.

The tendency for the forms diversion of the Cu in the two soils remained relatively unchanged as the time increase of incubation. However, there was a small alteration in all content forms by the 60th day with slightly increase of residual Cu versus decrease of exchangeable and carbonate Cu. The observed relatively no change in Cu forms between the two periods meant that aging would not affect the speciation proportion of Cu. However, the slightly increase of Cu proportion in RS fraction as a result of incubation time increased would keep Cu in a stable form in this fraction with little fluctuation within incubation period.

The redistribution of Pb forms after 60 days was noticed for the two soils. The content of the

exchangeable and carbonate Pb showed a small change, while the organic matter Pb was decreased at the end of incubation period. The remarkable reduction in organic fraction Pb may be due to decomposition of organic matter binding Pb within 60 days of incubation period. The residual Pb continued to increase, up to 63.4% and 47.41% for calcareous and sandy soils, respectively. Apparently, the increasing of residual fraction was mainly from the decreasing of organic fraction.

The effect of incubation period on Ni fractionation was considerable especially for sandy soils. As seen in Table 2, Ni residual fraction was increased significantly as incubation time finished, and this increase was arisen from the decrease of all fractions of NORS. For instance, Ni- residual fraction was increased to reach 92.64% and 91.27% whereas NORS were decreased till 7.36% and 8.73% for calcareous and sandy soils, respectively. The observed fluctuation of Ni RS and NORS fractions could be elucidated by the metals exchangeable between the RS and NORS fractions during the entire period of incubation. many factors could control metal conversion and allocation in soil system, and in this study, decrease of organic fraction-Ni as the increase of incubation time may be attributed to decomposition of metal Bound to organic matter in the amended soils, causing an increase in further fractions such as residual fraction. Finally, the redistribution of Pb and Ni after 60 days was towards more chemically stable and less bioavailability.

Metals desorption vs time

The effect of time during the 5th cycle (60 days incubation) on Cu, Pb, and Ni desorption using DTPA extractant from calcareous and sandy soils non-amended (control) and amended with both bulk and nano-sized WTR are shown in Fig. 2. For control soils, the desorbed amount of the three metals from both soils was decreased as a results of the incubation time increased. An almost linear curve of Cu and Pb release with time was noticed in both soils. On contrast, Ni release versus time was biphasic which characterized by a fast desorption reaction followed by a much slower rate. The higher amounts of all metals released were found for sandy soil rather than calcareous soil which could refer to higher calcium carbonate and OM content of the calcareous soil than of sandy soil. Carbonate fraction can substantially immobilize heavy metals by providing an surface adsorbing or buffering pH at values where metals hydrolyzes and precipitation can occur (Moral et al., 2005). Moreover, soil organic matter can

Table 2. Percentage of Cu, Pb, and Ni forms after first and fifth incubation cycles in the two studied soils amended with 0, 0.1 and 0.3% nWTRs

nWTRs Rate %	Incubation cycle	Metal forms (%)									
		Calcareous					Sandy				
		Exch	carb	Ox	OM	Res	Exch	carb	Ox	OM	Res
Cu											
0	First	5.67±0.45 ^a	17.39±0.88 ^a	13.17±0.71 ^b	15.95±0.83 ^b	47.82±0.81 ^a	9.67±0.83 ^b	6.47±0.51 ^a	29.82±0.76 ^b	32.67±0.76 ^b	21.36±0.83 ^a
	Fifth	5.312±0.23 ^a	16.932±0.43 ^a	17.784± ^b	18.531±0.67 ^a	41.441±0.4 ^b	11.134±0.7 ^a	7.134±0.41 ^a	33.654±0.91 ^a	35.976±0.4 ^a	12.102±0.5 ^b
0.1	First	2.60±0.4 ^a	8.43±0.72 ^a	7.83±0.95 ^a	9.43±0.55 ^a	71.71±0.7 ^b	5.37±0.7 ^a	3.19±0.48 ^a	15.34±0.9 ^a	19.79±0.8 ^a	56.31±0.7 ^b
	Fifth	1.93±0.71 ^a	6.92±0.48 ^b	6.89±0.63 ^a	9.02±0.85 ^a	75.24±0.5 ^a	4.43±0.49 ^a	2.36±0.67 ^a	14.99±0.7 ^a	19.29±0.8 ^a	58.93±0.69 ^a
0.3	First	1.086±1.13 ^a	2.77±0.76 ^a	5.84±0.83 ^a	4.53±0.51 ^a	85.77±0.7 ^a	2.47±0.5 ^a	1.81±0.71 ^a	8.44±0.83 ^a	9.02±0.51 ^a	78.27±0.7 ^b
	Fifth	0.67±0.83 ^a	1.34±0.71 ^b	5.06±0.83 ^a	4.13±0.51 ^a	88.8±0.88 ^a	1.89±0.51 ^a	0.68±0.76 ^b	8.14±0.83 ^a	8.67±0.71 ^a	80.62±0.83 ^a
Pb											
0	First	3.20±0.76 ^b	22.7±0.85 ^b	15.90±0.79 ^b	13.7±0.76 ^b	44.5±0.85 ^a	4.80±0.76 ^b	14.5±0.83 ^a	35.1±0.51 ^b	11.6±0.76 ^b	34.00±0.85 ^a
	Fifth	5.7±0.21 ^a	24.87±0.88 ^a	18.98±0.41 ^a	15.17±0.80 ^a	35.28±0.14 ^b	9.2±0.61 ^a	15.94±0.21 ^a	38.65±0.61 ^a	13.03±0.76 ^a	23.18±0.71 ^b
0.1	First	1.2±0.71 ^a	9.34±0.91 ^a	22.34±0.82 ^a	8.17±0.78 ^a	58.95±0.74 ^b	1.8±0.75 ^a	5.04±0.88 ^a	41.85±0.71 ^a	5.91±0.79 ^a	45.4±0.79 ^b
	Fifth	0.98±0.69 ^a	9.01±0.81 ^a	20.42±0.81 ^b	6.56±0.59 ^b	63.03±0.49 ^a	1.59±0.62 ^a	4.87±0.69 ^a	40.45±0.82 ^a	3.76±0.95 ^b	49.33±0.66 ^a
0.3	First	0.5±0.76 ^a	5.31±0.78 ^a	27.51±0.85 ^a	7.32±0.79 ^a	59.36±0.74 ^b	0.3±0.76 ^a	4.17±0.85 ^a	47.39±0.79 ^a	3.64±0.76 ^a	44.5±0.85 ^b
	Fifth	0.48±0.79 ^a	5.11±0.76 ^a	26.45±0.7 ^a	4.56±0.85 ^a	63.4±1.13 ^a	0.23±0.76 ^a	4.04±0.85 ^a	46.76±0.76 ^a	1.56±0.83 ^b	47.41±0.51 ^a
Ni											
0	First	2.96±0.96 ^a	22.34±1.04 ^a	18.82±1.14 ^b	6.72±0.83 ^a	49.07±1.14 ^a	4.39±1.14 ^a	16.43±0.83 ^a	23.43±1.13 ^b	11.64±1.15 ^a	44.11±1.12 ^a
	Fifth	3.54±0.86 ^a	23.07±0.51 ^a	20.76±0.11 ^a	7.04±0.98 ^a	45.59±0.17 ^b	5.23±0.83 ^a	16.87±0.81 ^a	25.98±0.99 ^a	11.87±0.71 ^a	40.05±0.71 ^b
0.1	First	0.41±0.81 ^a	12.12±0.66 ^a	9.74±0.67 ^a	2.01±0.74 ^a	75.72±0.71 ^b	2.01±0.71 ^a	8.12±0.97 ^a	14.63±0.88 ^a	6.86±0.71 ^a	68.38±0.77 ^b
	Fifth	0.28±0.87 ^b	10.31±0.82 ^b	7.34±0.87 ^b	1.43±0.88 ^a	80.64±0.97 ^a	1.89±0.98 ^a	7.01±0.59 ^a	12.67±0.84 ^b	5.64±0.96 ^a	72.79±0.72 ^a
0.3	First	0.18±0.04 ^a	5.31±0.76 ^a	4.52±1.13 ^a	1.81±0.85 ^a	88.18±1.04 ^b	0.92±1.14 ^a	3.15±0.83 ^a	5.73±1.14 ^a	3.87±1.15 ^a	86.33±1.13 ^b
	Fifth	0.01±0.04 ^b	3.56±1.13 ^b	3.12±1.14 ^a	0.67±0.83 ^a	92.64±1.15 ^a	0.76±1.14 ^a	2.12±0.83 ^b	3.64±1.13 ^b	2.21±1.16 ^b	91.27±0.85 ^a

All values are average of three replications. Means within a (vertical) column for both incubation time followed by the same letter do not differ significantly by the Duncan's multiple range test ($p < 0.05$).

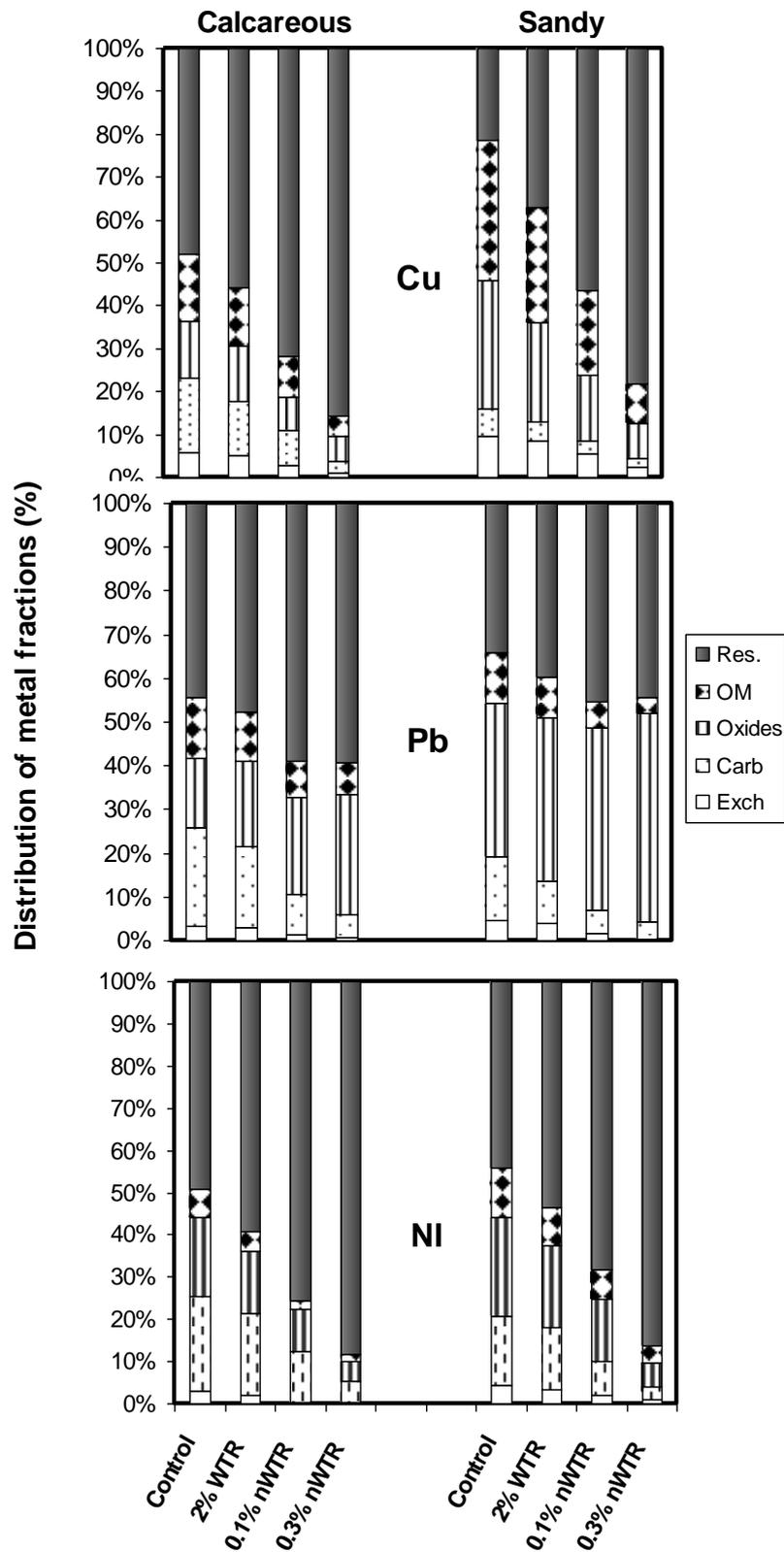


Fig .1. Relative percentage of Cu, Pb and Ni fractions for the two studied soils treated with biosolids (3 %, w/w) and amended with .WTR/nWTR. WTR, water treatment residual; nWTR, water treatment residual nanoparticles

strongly sorb heavy metals causing reducing their mobility in soil (Adriano, 2001). Among the three metals studied in both soils, Ni showed the least amount of desorbed metal followed by Pb while the higher amount of desorbed metal was for Cu. The low amount of desorbed Ni from both soils relative to other both metals was coincide with the data obtained from metals mobility index which showed the lower mobility index of Ni comparing with the other metals (Data not shown). This finding indicates the higher affinity of alkaline soil to sorb Ni than Cu and Pb which may be attributed to the higher ionic potential of Ni (2.6) than for Cu (2.5) and Pb (1.9) (Kabata-Pendias and Pendias, 2001). Furthermore, Kabata-Pendias and Pendias (2001) demonstrated that the ability of metal for precipitation can be increased as the increase of metal ionic potential.

The amount of desorbed Cu, Pb, and Ni from both soils was significantly decreased after application of bulk WTR and nWTR (Fig 2). This reduction in metals desorption was more intense in nWTR treatment especially at high treatment rate. For instance, in 0.30% nWTR at the first 12 days the Cu, Pb, and Ni desorbed from calcareous soil decreased by 70.23, 74.04, and 70.14, respectively- comparing with each own control. Clearly, nWTR application increased the sorbed metals onto the active surfaces of this nano-sized residuals leading to decreasing movement of metals towards solution. The high content of non-crystalline Fe/Al-(hydr)oxides, and Si-oxide of nWTR that proved from previous study of Elkhatib et al. (2015a)- using EDX and X-ray diffraction analysis- could be responsible for the high ability of metals towards nWTR-surface reaction sites. The strong bonding between heavy metals -including Pb, Cu, and Ni- and metal-oxides was found using molecular-scale X-ray spectroscopic tool which elucidated chemo-sorption reaction between metal and oxide-surfaces followed by metal precipitation in hydroxide form (Brown and Parks 2001; Sparks, 2001). Furthermore, other studies showed that heavy metals demonstrated desorption hysteresis process on goethite (Grossl and Sparks, 1994; Barrow et al., 2012). This results reflect the capability of nWTR holding amorphous iron, aluminum (hydr)oxides to immobilize studied metals in contaminated soils.

Desorption kinetic models

The desorption data were modeled for further description of the effectiveness of WTR/nWTR treatment with time on the three metals desorption process from both soils. The applied kinetic models are Elovich (Elkhatib and Hern, 1988), parabolic diffusion (Laidler, 1965), power function (Elkhatib et al., 1992), first order, and second order equations. The best fit of these models for the experimental desorption data was setup according to the highest coefficient of

determination (R^2) and the lowest standard error (SE) values. The high coefficient of determination and low SE values of parabolic diffusion and Elovich equations indicates that both models can successfully describe all desorption kinetic data. In contrary, power function, first order, and second order equations failed to express the all kinetic data which attributed to either high SE values of power function or low R^2 and high SE values of first and second order equations (data not shown). Table 3 displays the values of kinetic parameters for the two fit models used to describe the desorption kinetic data.

1-Intraparticle diffusion model

The plot of the Weber and Morris intraparticle diffusion model (metal desorbed versus $t^{0.5}$) for the desorption of Cu, Pb, and Ni from control and WTR/nWTR amended both soils gives a straight line but it does not pass through the origin; consequently intraparticle diffusion is not the sole rate-limiting step in the overall desorption process.. These plots are shown in Fig 3 for sandy soils-as example. The intraparticle diffusion rate constant (k_d , $\mu\text{g g}^{-1} \text{min}^{-1/2}$) was determined from the slope of the linear curve. This k_d value is considered a measure of the desorption rate of metals. The k_d value was lower for nWTR-treated soils comparing with other treatments (control and bulk WTR) with more pronounced at high rate (0.3%) as seen in Table 3. The low metal desorption rate from nWTR-treated soils could be due to specific adsorption on high energy sites of nWTR. Moreover, the intercept of the linear plot indicates an thought about boundary layer thickness which increase with the increase of the intercept (Weber and Morriss, 1963; Bayramoglu et al., 2009). The boundary layer thickness was significantly decrease as a results of nWTR treatment which indicate the contribution of the nWTR-surface sorption in the rate controlling step.

2-Elovich model

The plot of q (the amount of metal desorbed) against $\ln t$ gives a straight line with the slope of $(1/\beta)$ and intercept of $(1/\beta)\ln(\alpha\beta)$. where α is the initial desorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is related to the extent of surface coverage (mg g^{-1}) and activation energy for chemisorptions. The Elovich parameters (β , α) are calculated from the slope and intercept of the linear plot. As seen in Table 3, the initial desorption rate values ($\ln \alpha$) were low for all nWTR rates indicating increase of the rate of metal chemisorption (Elkhatib et al., 1992, 2001; Loukidou et al., 2004); consequently reduces the rate of metal release from nWTR-surfaces of treated soils into the solution.

Table 3. Kinetic parameters of Cu, Pb, and Ni desorption from calcareous and sandy soils treated with .WTR/nWTR

Treatment	Calcareous				Sandy			
	Parabolic Diffusion model							
	$q_t = a + k_d t^{1/2}$							
	k_d	a	R ²	SE	k_d	a	R ²	SE
	Cu							
0% WTR	1.45	36.44	0.99	0.0128	1.00	50.74	0.99	0.05489
2% WTR	0.97	24.29	0.99	0.0124	0.67	33.83	0.99	0.00987
0.1% nWTR	0.94	16.18	0.98	0.0223	0.45	27.19	0.97	0.00976
0.3% nWTR	0.24	10.18	0.99	0.0431	0.28	15.95	0.99	0.013421
	Pb							
0% WTR	3.09	33.62	0.99	0.00789	4.28	52.72	0.97	0.003561
2% WTR	1.93	21.01	0.99	0.0121058	2.85	33.74	0.95	0.02467
0.1% nWTR	1.71	16.07	0.99	0.1031	1.69	20.41	0.97	0.03410
0.3% nWTR	0.85	8.76	0.98	0.00913	1.31	14.37	0.97	0.00341
	Ni							
0% WTR	1.74	16.31	0.98	0.1139	2.55	27.17	0.98	0.0210584
2% WTR	1.09	10.19	0.98	0.001159	1.60	16.98	0.98	0.0075
0.1% nWTR	0.71	6.62	0.97	0.0560	1.05	10.99	0.96	0.1098
0.3% nWTR	0.53	4.91	0.97	0.00921	0.82	7.93	0.99	0.00973
	Elovich model							
	$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$							
	$\ln\alpha$	β	R ²	SE	$\ln\alpha$	β	R ²	SE
	Cu							
0% WTR	42.43	0.26	0.97	0.0154274	54.89	0.38	0.96	0.1006
2% WTR	28.32	0.39	0.97	0.00322	36.51	0.57	0.96	0.01997
0.1% nWTR	20.13	0.40	0.97	0.01459	28.73	0.86	0.92	0.002387
0.3% nWTR	10.56	1.53	0.98	0.002667	16.61	1.33	0.99	0.0876
	Pb							
0% WTR	45.53	0.12	0.96	0.001936	68.38	0.09	0.93	0.003227
2% WTR	28.77	0.19	0.96	0.045748	43.17	0.14	0.93	0.04398
0.1% nWTR	23.06	0.22	0.97	0.004022	26.99	0.23	0.88	0.000681
0.3% nWTR	12.26	0.45	0.95	0.0316	19.67	0.29	0.93	0.004347
	Ni							
0% WTR	23.69	0.22	0.98	0.001751	37.59	0.15	0.98	0.0038327
2% WTR	14.91	0.34	0.98	0.002387	23.74	0.24	0.98	0.00461
0.1% nWTR	9.97	0.49	0.94	0.001159	15.64	0.35	0.97	0.001332
0.3% nWTR	7.18	0.67	0.94	0.021058	14.23	0.35	0.98	0.002833

R², determination coefficient; SE, standard error of estimate; WTR, water treatment residual; nWTR, water treatment residual nanoparticles; q, metal desorbed (mg kg⁻¹); α, the initial desorption rate (mg g⁻¹ min⁻¹), β, a constant related to the extent of surface coverage (mg g⁻¹); k_d, the intraparticle diffusion rate constant (μg g⁻¹ min^{-1/2}); a, a constant

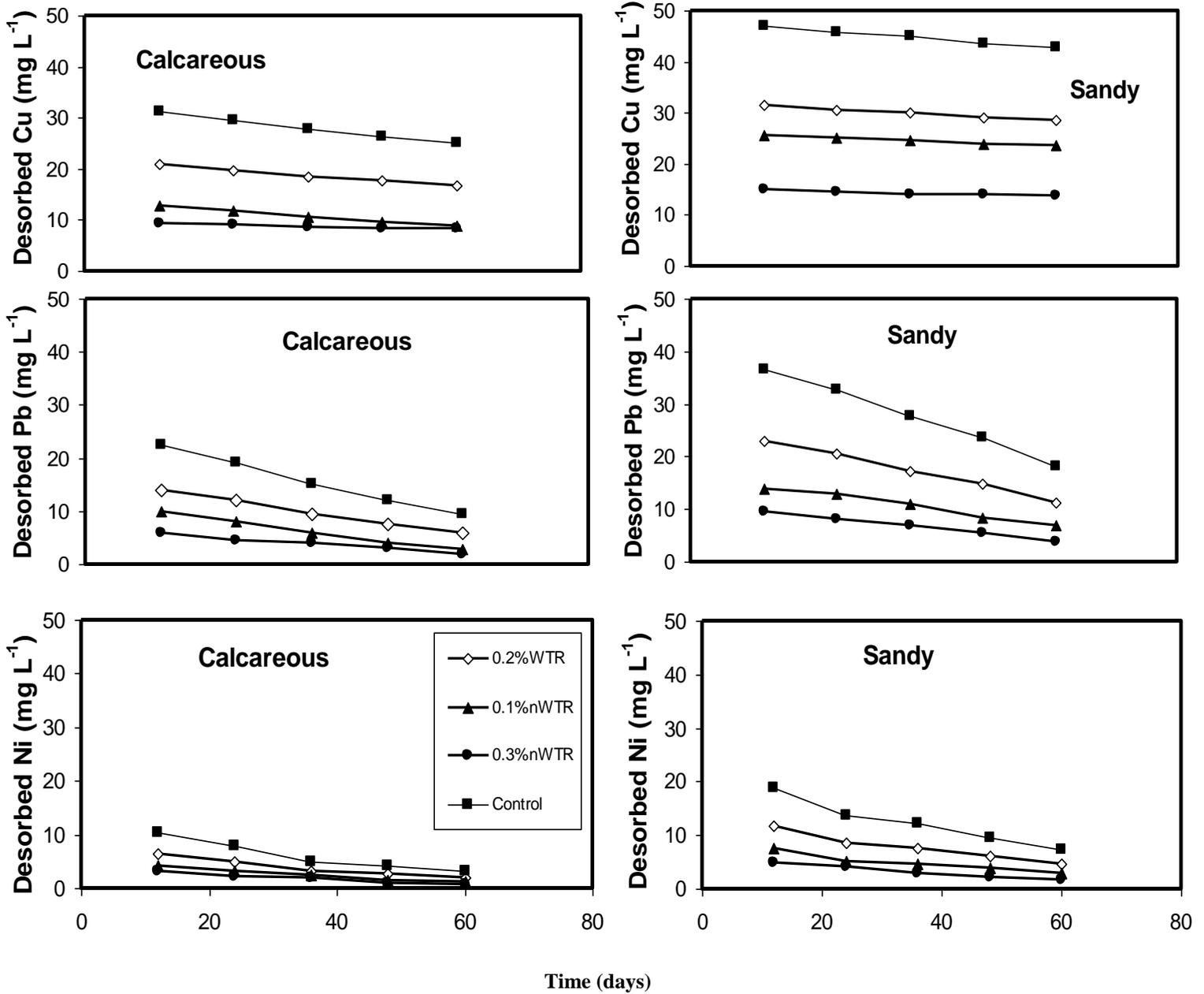


Fig. 2. Metals desorption during 60 days incubation period from the two studied soils treated with biosolids (3 %, w/w) and amended with .WTR/nWTR. WTR, water treatment residual; nWTR, water treatment residual nanoparticles

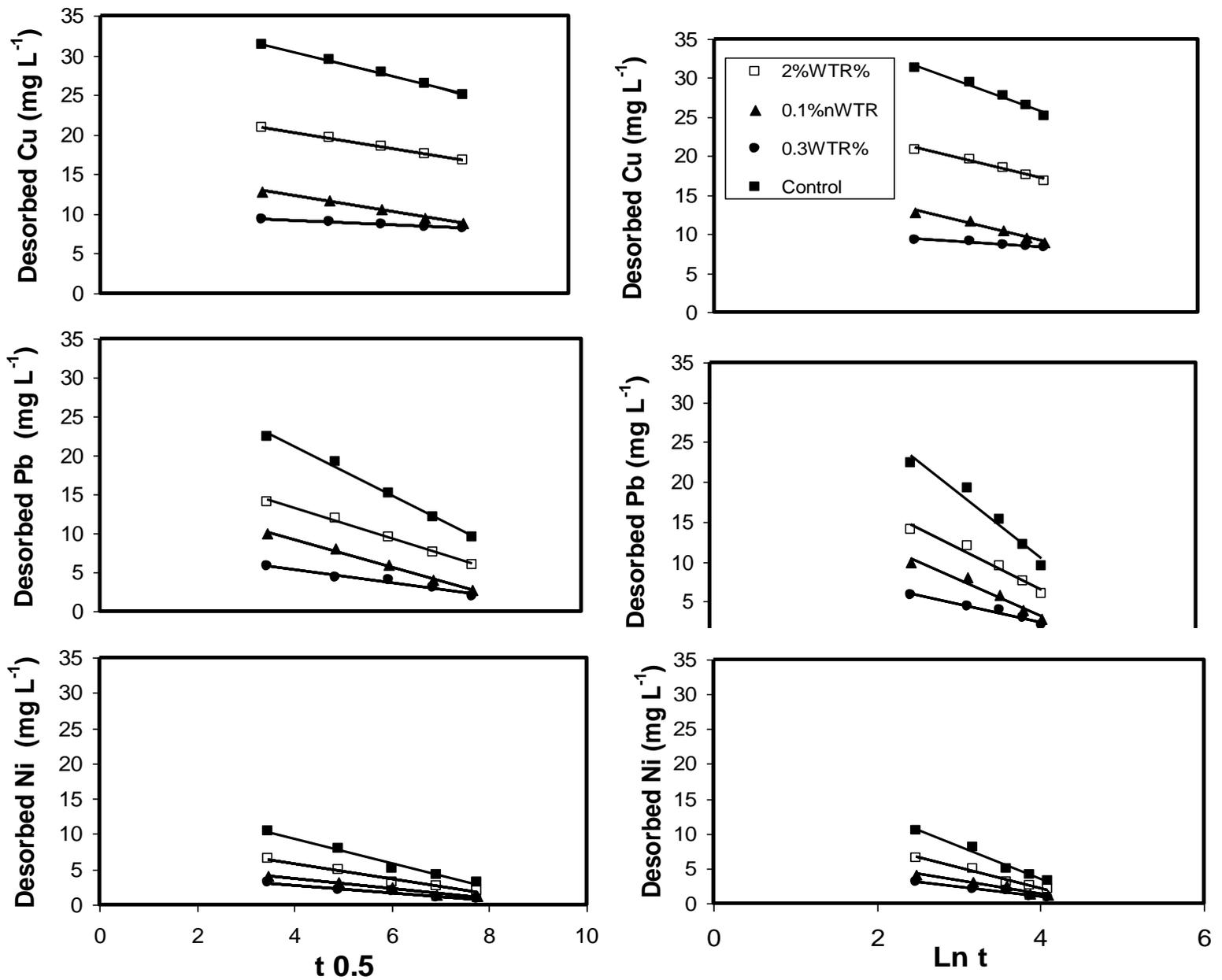


Fig. 3. Intraparticle diffusion (left graphs) and Elovich kinetic plots (right graphs) for metals desorption from calcareous soil treated with biosolids (3 %, w/w) and amended with .WTR/nWTR. WTR, water treatment residual; nWTR, water treatment residual nanoparticles

CONCLUSION

The effect of 60 days incubation period of biosolid-treated control soils on metals mobility and availability was examined as discussed from metals-fractions redistribution and mobility index findings. Thus, the redistribution of metals over the 60 days incubation period was towards more mobility and availability with more pronounced for Cu in sandy soil and less evident for Ni. However, the increase of Cu and Pb in oxide and organic fractions for both soils over this period could recompense this Pb/Cu-available increase.

The nWTR amendments in both biosolid treated soils were efficient to increase both three metals- RS fraction and Pb-oxide fraction with further increase of Pb/Ni-RS fraction over the 60 days incubation period. Although a little effect of aging in case of Cu was found, the slightly increase of Cu proportion in RS fraction as a result of incubation time increased would keep Cu in a stable form in this fraction with little fluctuation within incubation period. Furthermore, the DTPA-desorbed metals within the five wetting drying cycles were significantly decreased as a results of nWTR addition. Obviously, these results indicate the potential of using nWTR as a land amendment to mitigate heavy metals hazardous impacts in biosolids treated soils; so, it is recommended to added nWTR with biosolids once land application of biosolid.

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الملخص العربي

إعادة التوزيع وحركية التحرر لبعض العناصر الثقيلة في الأراضي المعاملة بالحماء والمضاف إليها مخلفات معالجة مياه الشرب النانومترية

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العناصر الى صورة أقل ثباتا في مكونات التربة وأكثر صلاحية للامتصاص بواسطة النبات وكان هذا التأثير أكثر وضوحا في عنصر النحاس في الاراضى الرملية وأقل تأثيرا في عنصر النيكل.

إضافة مخلفات معالجة مياه الشرب النانومترية إلى الاراضى الجيرية والاراضى الرملية أدى إلى زياده معنويه في صور العناصر الاكثر ثباتا في التربة والاقل صلاحية للامتصاص بواسطة النبات مع زيادة هذا التأثير بزيادة مدة التحضين وبالإضافة الى ذلك حدث إنخفاض ملحوظ في كمية العنصر المتحرر بمستخلص DTPA (المعبر عن صلاحية العنصر للامتصاص بواسطة النبات) خلال الخمس دورات من الابتلال والتجفيف كنتيجة لاضافة مخلفات معالجة مياه الشرب النانومترية.

تشيرالنتائج النهائية إلى إمكانية استخدام هذه المخلفات النانومترية للتقليل من الأثار الضاره للعناصر الثقيله في الاراضى المعاملة بالحماء، لذا فهذه الدراسه توصى بخلط الحماء مع مخلفات معالجة مياه الشرب النانومترية عند الاستخدام فى الاراضى المختلفه.

أجريت هذه الدراسه لبيان تأثير مخلفات معالجة مياه الشرب النانومترية (المتحصل عليها من محطات تنقية مياه الشرب والتي تم تحويلها معمليا إلى مواد نانومترية عن طريق عملية الطحن) وذلك عند ثلاث مستويات إضافة (صفر، ٠,١%، ٠,٣%) لنوعين من الاراضى المصريه (الجيرية والرملية) المعاملة بالحماء عند مستوى إضافة (٠,٣%) على التغير فى صورة العنصر (مدى ارتباط العنصر بمكونات التربة المختلفه) محل الدراسه (النحاس، الرصاص، النيكل) وكذلك على تحرر هذه العناصر إلى المحلول المائى للتربة. هذه الاراضى المعاملة بالحماء والمضاف إليها مخلفات معالجة مياه الشرب النانومترية تم تحضينها لمدة ستين يوما على خمس دورات متتاليه من الابتلال والتجفيف كل دوره إثتى عشر يوما وذلك لبيان تأثير زمن التحضين على صورة العنصر وذائبيته.

أوضحت نتائج الدراسه الاتى:

- زيادة فترة التحضين من ثلاثين الى ستين يوما للاراضى المعاملة بالحماء والغير مضاف اليها مخلفات معالجة مياه الشرب (الكنترول) أدى الى تغير واضح فى تحويل صور