

Effects of Citrus Peel Amendment on the Mobility of Heavy Metals in Contaminated Soil

B. Lorestani^{1*}, M. Cheraghi¹ and H. Merrikhpour²

¹Department of Environment, Islamic Azad University, Hamedan branch, Hamedan, Iran.

²Department of Chemistry, University of Sayyed Jamaledin Asadabadi, Asadabad, 6541835583, Iran.

Authors' contributions

This work was carried out in collaboration between all authors. Author BL is corresponding author who managed the literature searches and produced the initial draft. Author MC wrote the protocol and interpreted the data. Author HM anchored the field study, gathered the initial data and performed preliminary data analysis. All authors read and approved the final manuscript

Article Information

DOI: 10.9734/ARRB/2015/11512

Editor(s):

(1) Hans Vliegthart, Bijvoet Center, Division Bioorganic Chemistry, Utrecht University, Utrecht, The Netherlands.

(2) George Perry, Dean and Professor of Biology, University of Texas at San Antonio, USA.

Reviewers:

(1) Anonymous, Brazil.

(2) Anonymous, Benue State University, Nigeria.

Complete Peer review History: <http://www.sciencedomain.org/review-history.php?iid=795&id=32&aid=6891>

Original Research Article

Received 20th May 2014
Accepted 8th September 2014
Published 13th November 2014

ABSTRACT

To estimate the effect of aging on the mobility of heavy metals in soil, relationships between mobility of metals in soil and time after contamination were investigated. Copper, nickel and zinc were added as chloride solution to soil sample. Citrus peel as soil amendments was used at the rate of 5% to immobilize copper, nickel and zinc in contaminated soil. The soils were incubated at field capacity for 3 h, 1, 3, 7, 14, 21 and 28 days at 25°C.

Mobility of copper, nickel and zinc from control soils and soils amended with citrus peel were studied with the aid of reduction of metals concentration in the exchangeable fraction.

Results indicated that the citrus peel reduced the exchangeable fraction of metals in contaminated soil after 28 days. Application of citrus peel amendment with acidic pH value showed the low immobilizing efficiency of copper, nickel and zinc in the beginning of incubation time in this study due to decrease in soil pH.

Batch adsorption of copper, nickel and zinc was conducted to evaluate the effect of contact time, from aqueous solution to understand the mechanism of sorption involved. Fit of the sorption

*Corresponding author: Email: saba12ir@yahoo.com;

experimental data was tested on the pseudo-first and pseudo-second-order kinetics mathematical equations, which was noted to follow the pseudo-second-order kinetics better, with coefficient of correlation ≥ 0.99 .

Keywords: Citrus peel; contamination; heavy metal; in situ immobilization; kinetic models.

1. INTRODUCTION

The environment can become polluted with organic and inorganic chemicals as a result of intended, accidental or naturally occurring events such as manufacturing processes, mineral extraction, poor environmental management and waste disposal activities, application of fertilizer, illegal dumping of wastes, leaking underground storage tanks, abandonment of mines and other industrial activities [1].

Given the widespread distribution of heavy metals in soil, it is desirable to develop cost-effective remediation strategies for these metals. There are relatively few fully developed, in situ methods available for remediation of metals in soils, and often, remediation at a given site consists of traditional alternatives such as excavation (for treatment/disposal) or containment. However, excavation of metal-contaminated soils may be impracticable due to the excessive cost involved, the magnitude (area, depth, volume) of the soil contamination, and the degree of disruption incurred at the site. Containment alternatives, such as soil caps, are often inconsistent with the desired end use for the site and may be viewed negatively by the regulatory community and the public. As with any remediation, the overall objective of an in situ remediation approach is to create a final solution that is protective of human health and the environment. Metal contamination of soils can represent a threat to human and ecological health through direct contact, can be a source for metal transport to critical resources (e.g., groundwater and surface water bodies), and can hinder the ability of the soil to support vegetation and a functioning ecosystem.

As a result, in situ remediation of metal-contaminated soils typically concerns reduce metal leaching and metal bioavailability to human and ecological receptors. At many sites, there is a potential for metals to be leached from soils by infiltrating water, spreading the contamination and potentially affecting groundwater and other down gradient resources.

The soil environment is able to store, transform and remove pollutants through a combination of

biological, chemical and physical processes [1]. But, a suitable method of mitigation is required to render pollutants less mobile and harmful to receptors; this can potentially be achieved by the addition of amendments, to contaminated soils. Bio-solids have been increasingly used in soil management for improving soil quality. The initial measurements of contaminants during site investigation are usually total concentrations of contaminants. However, it is usually the "bioavailable" fraction that is relevant to whether the contaminants present in a soil pose a hazard or not. Bio-solids applications have been shown to be capable of reducing the bioavailability and phytotoxicity of lead, cadmium, and zinc in contaminated soils [2,3].

The land application of bio-solids significantly increases the organic matter content of the soil, enhancing its adsorptive capacity for heavy metals [4,5]. The organic matter adsorbs to inorganic soil constituents, providing additional complexation sites for heavy metals. However, much of the organic matters added to the soil as a result of the land application of bio-solids eventually decompose [6]. Addition of organic matter amendments is a common practice for immobilization of heavy metals and soil amelioration of contaminated soils [7]. The effect of organic matter amendments on heavy metal bioavailability depends on the nature of the organic matter, their microbial degradability, as well as on the particular soil type and metals concerned [8,9]. Cochrane et al. [10] investigated the use of three biosorbents (crab carapace, macroalgae *Fucus vesiculosus*, peat) for the removal of copper from aqueous media. The maximum adsorption capacity values were 79.4, 114.9 and 71.4 mg g⁻¹ for crab carapace, *F. vesiculosus* and ion-exchange resin, respectively. In other study, Abdel Salam et al. [11] showed the peanut husk can adsorb copper and zinc from wastewater. Peanut husk charcoal can adsorb metal in average of 0.36 mg g⁻¹. A strange adsorbent material (straw) was used by Kumar et al. [12] in order to remove heavy metals from aqueous systems. The results of many biosorption studies vary widely because of the different criteria used by the authors in searching for suitable materials.

Certain waste products, natural materials and biosorbents have been tested and proposed for metal removal. It is evident from the discussion so far that each low-cost adsorbent has its specific physical and chemical characteristics such as porosity, surface area and physical strength, as well as inherent advantages and disadvantages in wastewater treatment. In addition, adsorption capacities of sorbents also vary, depending on the experimental conditions.

There is evidence that in bio-solid amendments soils, heavy metals remain in the top layer of the soil. Other researchers report either no or little movement of metals into the sub layers of the soil profile [13-15]. While soils tend to bind the various species of heavy metals to some degree, the specific mechanisms, and thus both the degree and strength of retention, may vary greatly and may change temporally. The binding mechanism will therefore influence the extent to which contaminant transport is attenuated and the availability of contaminants for uptake by biological organisms.

Sequential extraction procedures have been used by many researchers in order to study the forms of heavy metals in soils. Chang et al. [16] found that land application of bio-solids tended to increase the fraction of total metal found in every fraction, especially the organic fractions of the soil. These results were substantiated by Sims and Une and Taylor et al. [17,18]. Swami and Buddhi reviewed the removal of toxic metals including Chrome, Copper, Mercury and nickle from industrial waste water using the agricultural by-products [19]. Compared to the conventional processes for the metal removal in waste water, the device was more cost effective. Also Inbaraj and Sulochana demonstrated fruit shell of *Terminalia catappa* as a useful sorbent for heavy metal removal from waste water [20].

The present study follow the objective to broaden and increase the knowledge of the effect of citrus peel additives on the quantity of exchangeable forms of copper, nickel and zinc in soil.

2. MATERIALS AND METHODS

2.1 Soil Samples

The native soil sample (Typic xerochrepts) was taken from the 0 to 30 cm layer of agricultural soil (X:287441.21 Y:3819829.39 WGS 1984 UTM Zone 39N). The soil was air-dried and passed through a 2 mm sieve before being stored in polyethylene bags. The chemical and physical

properties [21] of the studied soil are shown in (Table 1).

2.2 Batch Sorption Studies

The batch sorption experiments were run by adding 0.5 g of biosorbent (citrus peel) to 25 ml of solutions containing heavy metal ions of desired concentrations (100 mg l^{-1}) for each metal at constant temperature ($25 \pm 0.1^\circ\text{C}$) in 50 ml polyethylene tubes. The tubes were shaken in an orbital shaker at 150 rpm from 10 min. to 24 h and solutions containing heavy metals were filtered through Whatman filter paper (No. 42). Blank samples (without bioasorbent) were prepared for all experiments to investigate copper, nickel and zinc sorption to tube walls and filters.

The percent metal ions removal (R , %) was calculated for each run by following expression:

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e were the initial and final concentration of metal ions in the solution, respectively.

2.3 Kinetic Model

The pseudo-first and second order kinetic models were used to describe the sorption kinetic data of cadmium, copper and zinc measured on sorbent [22]:

The linear form of the models is shown below

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the citrus peel (mg g^{-1}) at equilibrium and at time t , respectively. k_1 is the rate constant of first-order (min^{-1}), and k_2 is the rate constant of second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

2.4 Soil Amendment

The soil used in the experiment was artificially polluted by adding salts of copper, nickel and zinc using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 , to pollute the soil, respectively. All chemicals were

of the analytical grade purchased from Merck Company (Darmstadt, Germany).

For this, 0.8 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1.2 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.6 g ZnCl_2 were dissolved in 1 L distilled water separately and there after mixed uniformly with 1 kg soil. After uniform mixing, the suspensions were transferred to plastic boxes and left uncovered at ambient temperature for two weeks. Over the course of these two weeks, the soil samples lost their water content. The reason for leaving them to dry was to allow the test metal to stabilise and speciate before the experiment started.

The citrus peel was washed with distilled water; oven dried at 70°C and powdered with electric grinder, then mixed whit soil samples.

The citrus peel stabilized soil sample was prepared by adding 5% citrus peel (5 g citrus peel added to 100 g soil). The samples were incubated for 3 h, 1, 3, 7, 14, 21 and 28 days at 25°C. The appropriate amount of deionized water was added to bring the soil to the estimated field capacity. The samples were kept moist by adding distilled water as needed. All incubation experiments were carried out in duplicate. In order to investigate the heavy metals sorption mechanism onto soil, soil samples without citrus peel and artificially polluted with heavy metals were prepared as control soil and kept at the same condition of soil amended with citrus peel [23]. Also native soil sample without amended with heavy metals were prepared as investigate the heavy metal distribution in parent material.

After incubation the samples were air dried and ground through a 2 mm sieve.

2.5 Extraction Procedure

A standardized procedure with aqua regia was used to determine the total contents of heavy metals in soils (both amended and control) [24]. Exchangeable and Mobile fraction extractions extract was performed with 20 ml of 1 M NH_4OAc at pH 7 for 2 h at room temperature [25]. The copper, nickel and zinc Concentrations in the extracts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ES-710).

3. RESULTS AND DISCUSSION

3.1 Batch Sorption Experiment

The rate of sorption of copper, nickel and zinc by citrus peel was determined for different intervals

of time. The equilibrium was reached within 60, 90 and 120 min for copper, nickel and zinc respectively (Fig. 1). The uptake of metal ions, as a function of time, was noted to occur in two phases. The first phase involved a rapid uptake of metals during the first 30-60 min of the sorbate-sorbent contact, which was followed by a slow phase of metal removal spread over a significantly longer period of time until the equilibrium was reached. The two-stage sorption, the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature [26].

The rapid stage, furthermore, may last for several minutes to a few hours, while the slow one continues for several hours to a day [27]. The rapid phase is probably due to the abundant availability of active sites on the sorbent, whereas with the gradual occupancy of these sites the sorption process becomes less efficient during the slower phase [28].

To examine the controlling mechanism of the adsorption process, such as mass transfer and chemical reaction, the pseudo-first-order and the pseudo-second-order kinetics models were used to test the experimental data of copper, nickel and zinc by citrus peel.

A good linear plot of t/q_t against t for the pseudo-second-order kinetics model shows good fit on the model (Fig. 2). The low correlation coefficient value ($r^2 = 0.47, 0.52$ and 0.21 for copper, nickel and zinc respectively), as obtained for the pseudo-first-order model, indicates that sorption of studied metals did not follow the pseudo-first-order reaction.

The insufficiency of the pseudo-first-order model to fit the kinetics data could possibly be due to the limitations of the boundary layer controlling the sorption process. The experimental data were observed to fit well the pseudo-second order equation. The high correlation coefficient value ($r^2 = 0.99$), as obtained for the pseudo-second-order equation, was observed to be close to 1. This suggests that the process of sorption kinetics of copper, nickel and zinc by citrus peel follows the pseudo-second-order equation and the process controlling the rate may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [30].

Table 1. Some physical and chemical properties of native soil

Solution cations and anions (mg l ⁻¹)								% soil texture				EC (dS m ⁻¹)	pH
Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	PO ₄ ³⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Sand	Silt	Clay	Clay- loam		
32.0	45.2	9.6	26.2	3.3	95.6	22.3	69.4	35.0	28.5	36.5		0.452	7.76
Heavy metal distribution in native soil* (mg kg ⁻¹)				Total	EXCH	CARB	MNO	FEO	OM	RES			
Cu				22.0	2.6	3.7	1.2	2.1	5.3	7.1			
Ni				48.0	4.3	4.8	3.7	5.2	6.8	23.2			
Zn				83.0	4.5	5.8	6.7	7.9	6.3	51.8			

*EXCH: Soluble plus exchangeable, CARB: Carbonate bound, MNO: Mn oxide bound, FEO: Fe oxide bound, OM: Organic bound, RES: residual [29]

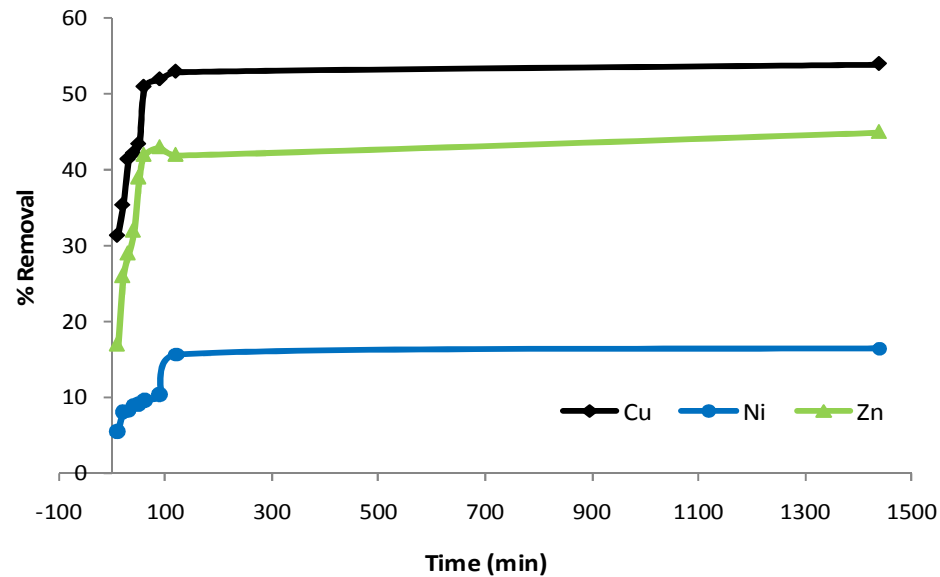


Fig. 1. Effect of contact time on the adsorption of copper, nickel and zinc onto citrus peel

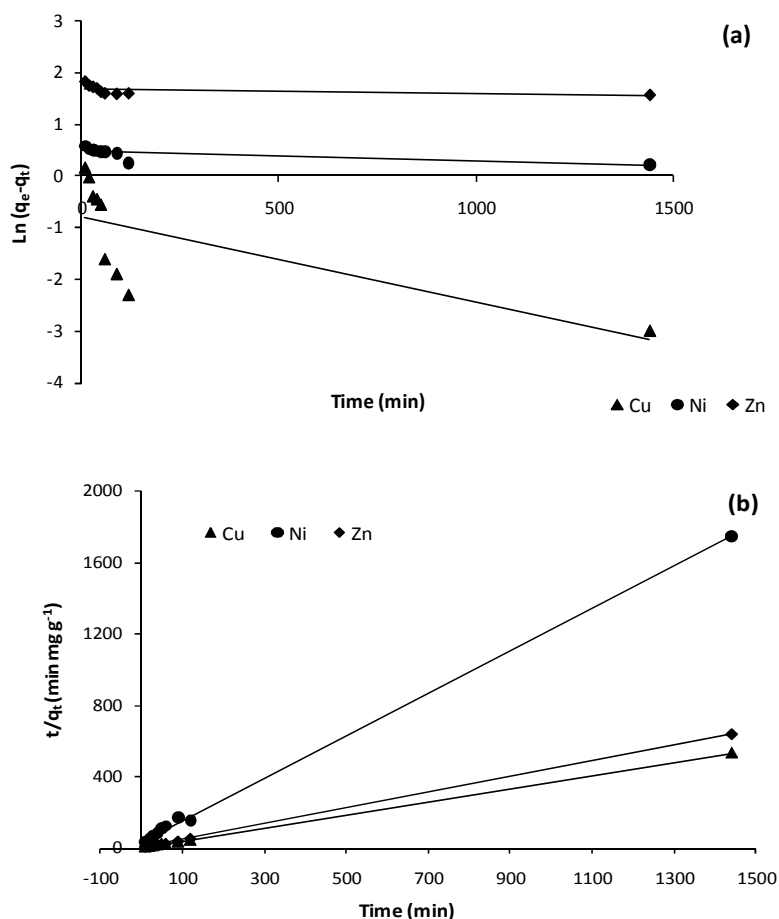


Fig. 2. Pseudo-first order (a) and pseudo-second-order (b) sorption kinetic of copper, nickel and zinc onto citrus peel

3.2 Incubation Experiments

The soils amended with citrus peel were analyzed after the for 3 h, 1, 3, 7, 14, 21 and 28 day incubation period and their properties were compared with those of the control soil. The pH values of the soils are listed in (Table 2). As can be seen, an addition of citrus peel resulted in a relative decrease of the pH values. The pH values play a crucial role in the mobility of metals in soils, as they govern directly the acid-base equilibria, and affect (indirectly) both the solution and surface complexation reactions of metal cations, ion-exchange and other metal-binding processes, as well as solubility and metal-binding ability of humic substances as main organic soil constituents.

Typically, the decrease pH values promote the solution of metal cations (including a surface precipitation, in some cases) and increase the

metal mobility (contents of easily extractable fractions) [31]. Introduced stabilization materials had a different influence on soil pH in respect to the nature of amendment and soil reaction [32]. Stabilizers exert an influence on physical and chemical properties of soil and metal by changing the conditions of soil environment to those more favorable for metal retention or precipitation.

The total (aqua regia extractable) contents of copper, nickel and zinc in the control soils and soils amended with citrus peel are listed in (Table 3) together with the results of the mobile fraction tests. As can be seen, the total content of copper, nickel and zinc were not affected significantly by an addition of citrus peel amendment, which is consistent with low contents of copper, nickel and zinc in the citrus peel.

Total metal concentration in the soil reflects the degree of contamination and natural differences in soil genesis. A comparison of the total metal levels with World Health Organization (WHO), United States Environmental Protection Agency (USEPA), and the Toxicity Characteristic Leaching Procedure (TCLP) presented in (Table 4). The data evidenced much enhanced levels for three metals than various standard values. Total nickel levels of native soil samples surpassed the limits set by the WHO, USEPA, and TCLP. The high concentration of nickel may cause toxicity not only to plants but also to humans [33].

The mobility's of the metals in soil samples were evaluated on the basis of the absolute and

relative content of fractions bound weakly to soil components. The relative index of metal mobility (mobility factor, MF) was calculated on the basis of the ratio of proportion of mobile to the total content of metals [34].

The MF for copper, nickel and zinc in citrus peel treatment was 0.15, 0.25 and 0.15 and in control soil was 0.19, 0.34 and 0.21 respectively. A comparative evaluation of mobilities of different metals evidenced maximum mobility index for nickel. The high MF values are interpreted as symptoms of relatively high lability and biological availability of respective metal in soils [35,36]. Moreover, the mobility index of the metals was not found to exceed 15% evidencing the high stability of these metals in the soil matrix.

Table 2. Mean pH values of the soil amended with citrus peel and control soil in different incubation time

	pH	
	Soil amended with citrus peel	Control soil
3 h	7.64	7.76
1 day	7.48	7.75
3 day	7.32	7.75
7 day	7.22	7.71
14 day	7.03	7.66
21 day	6.89	7.65
28 day	6.81	7.65

Table 3. Total and mobile fraction of copper, nickel and zinc (mg kg^{-1}) in control soils and soils amended with citrus peel in different incubation time. (Total copper, nickel and zinc of the native soil were 22.0, 48.0 and 83.0 mg kg^{-1} respectively)

	Soil amended with citrus peel			Control soil		
	Copper	Nickel (mg kg^{-1})	Zinc	Copper	Nickel (mg kg^{-1})	Zinc
Total	321.3	347.4	381.8	321.2	347.4	381.6
Mobile fraction						
3 h	110.2	185.2	147.3	104.5	173.6	130.8
1 day	100.3	189.6	135.1	102.4	169.5	130.4
3 day	91.2	149.3	110.6	95.4	150.7	122.6
7 day	81.2	123.7	90.5	88.9	137.9	103.1
14 day	65.8	107.8	74.3	79.5	133.6	95.6
21 day	53.4	95.4	68.4	70.3	128.5	89.2
28 day	46.9	88.3	60.5	64.1	119.6	81.7

Table 4. Comparison of total metal levels in native soil with various international standards

	Metal concentration (mg kg^{-1})	WHO	USEPA	TCLP
Copper	22.0	-	20	-
Nickel	48.0	20	10	5
Zinc	83.0	50	-	-

Rates of exchangeable fraction of metals were shown in (Figs. 3-5). Among metals, rates of exchangeable fraction were in the order of copper < zinc < nickel (There isn't any difference between the native and amended soil), reflecting their intrinsic chemical reactivity in soil. There was slight increase during the first days of incubation in citrus peel amended soil in contrast with control soil and then decrease overcome after the period for all three metals. It was concluded that decreasing the pH due to presence of citrus peel result in solution and availability of metals especially nickel. The mobile fraction properties depended on soil reaction, type of metal and properties of amendments [32]. It was concluded, therefore, that risk assessment of soil contamination can be accomplished by the determination of incubation time and pH of soils. According to Kumar et al., the optimum pH for nickel adsorption for all the husks is 5 to 5.5 [12]. The results of effect of pH on the removal of metals reveal that irrespective of the husk (adsorbent) metal ions were adsorbed. Also the results of Rieuwert et al. [37] studies showed that metal solubility tends to increase at lower pH and adsorption reactions become more important than precipitation and complexation reactions. As their results, adsorption reactions of Pb are significant at soil pH 3–5 and of Zn at pH 5–6.5. Precipitation and complexation reactions of both Pb and Zn predominate at soil pH 6–7. According to McLean and Bledsoe nickel does not form insoluble precipitates in soils and

retention for nickel is, therefore, exclusively through adsorption mechanisms [38]. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and is thus removed from the soil solution.

When the incubation time was prolonged metal concentration of the exchangeable fraction decreased, especially for copper in citrus peel amended soil. In control soil the decrease of metals in exchangeable fraction was less than citrus peel amended soil. The newly added copper existed mainly as exchangeable fraction, but After 7 day incubation, copper in exchange fraction decreased and after 28 day was 46.9%.

Sayed and Zayed investigated adsorption capacity and the effectiveness of s garlic and onion peels, in oil spill clean-ups [39]. It was found that the adsorption capacities were high for garlic and onion peels.

Wilson and Yang converted peanut shells with pyrolysis to activated carbons [40]. It was reported that shells could be used as an adsorbent for metal ions such as: cadmium, copper, lead, nickel and zinc.

Fitzmorris et al. [41] evaluated the removal of calcium, copper, chrome, lead, nickel, zinc, arsenic and selenium from solution using the fruit stone and showed the good adsorption of studied amendment.

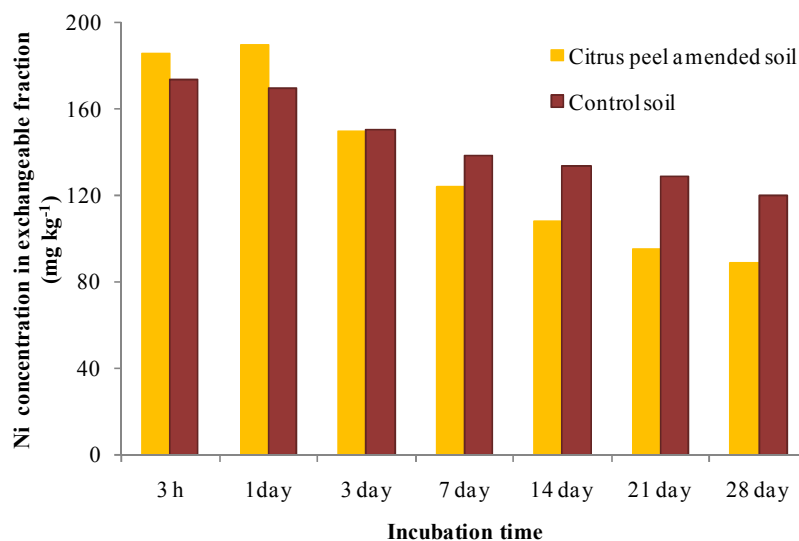


Fig. 3. Exchangeable fractionation of nickel in the citrus peel amended and control soils in different incubation time

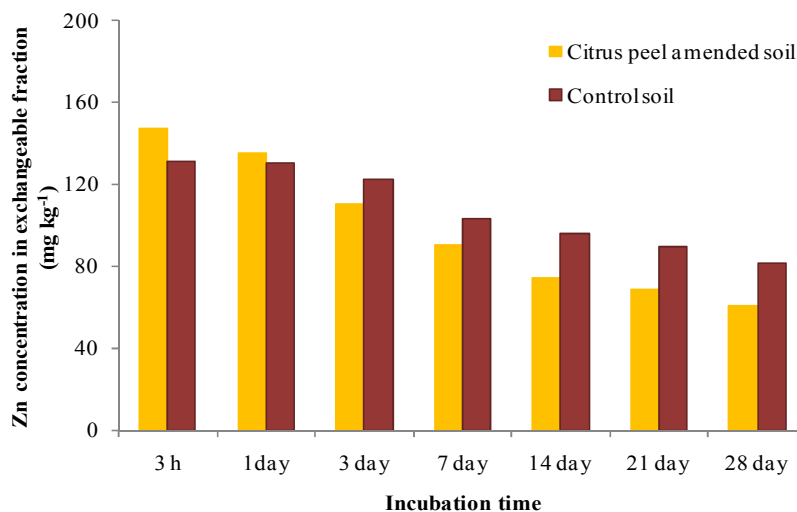


Fig. 4. Exchangeable fractionation of zinc in the citrus peel amended and control soils in different incubation time

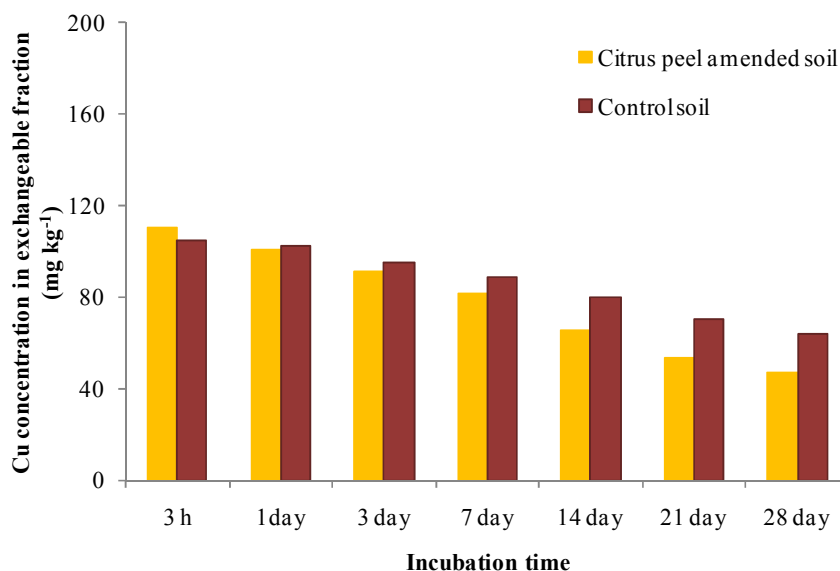


Fig. 5. Exchangeable fractionation of copper in the citrus peel amended and control soils in different incubation time

4. CONCLUSION

The application of citrus peel altered the mobile fraction of copper, nickel and zinc to less mobile fraction in contaminated soil in studied period (4 weeks). This resulted in a diminished uptake of metals to plants and lower leachability to ground water.

The citrus peel can be considered as an effective immobilization agent for remediation of copper,

nickel and zinc in contaminated soils in longer period, because in short time decrease in pH value of soil led to increase the mobile fraction of metals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. USEPA. U.S. Environmental Protection Agency. Quality Criteria for Water. EPA Publication 440/5-86-001. U.S. Gov. Prin. Office, Washington D.C; 1987.
2. Li YM, Chaney RL. Case studies in the field—Industrial Sites: Phytostabilization of zinc smelter-contaminated sites: The Palmerton case. In: Vangronsveld J, Cunningham SD. 6th ed. Metal contaminated soils: In situ inactivation and phytoremediation. Georgetown, TX: Springer-Verlag and R.G. Landes Company; 1998.
3. Basta NT, Gradwohl R, Snethen KL, Schroder JL. Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. *J. Environ. Qual.* 2001;30:1222–1230.
4. Karapanagiotis NK, Sterritt RM, Lester JN. Heavy metal complexation in sludge amended soil. The role of organic matter in metal retention. *Environ. Technol.* 1991;12:1107–1116.
5. Petrizzelli LG, Petronio BM, Gennaro AVMC, Liberatori A. Soil sorption of heavy metals as influenced by sewage sludge addition. *J. Environ. Sci. Health.* 1994;29:31–50.
6. McBride MB. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective *Environ Qual.* 1995;24:5–18.
7. Clemente EP, Schaefer CEGR, Novais RF, Viana JH, Barros NF. Soil compaction around *Eucalyptus grandis* roots: A micromorphological study. *Soil Res.* 2005;43:139–146.
8. Walker DJ, Clemente R, Roig A, Bernal MP. The effect of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. *Environ. Pollution.* 2003;22:303–312.
9. Walker DJ, Clemente R, Bernal MP. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere.* 2004;57:215–224.
10. Cochrane EL, Lu S, Gibb SW, Villaescusa I. A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *J. Hazard. Mater.* 2006;137:198–206.
11. Abdel Salam OE, Reiad NA, ElShafei MM. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *J Adv Res.* 2011;2:297–303.
12. Kumar A, Rao NN, Kaul SN. Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal—Preparation, characterization and application. *Bioresour. Technol.* 2000;71:133–142.
13. Chang AC, Wmeke LE, Page AL, Lund LJ. Heavy metals accumulation soils of in sewage sludge-treated. *J. Environ. Qual.* 1984;13:87–91
14. Williams DE, Vlarnis J, Pukite AH, Corey JE. Metal movement in sludge treated soils after six years of sludge addition: 1. Cadmium, copper, lead and zinc. *Soil Sci.* 1984;137:351–359.
15. Williams DE, Vlarnis J, Pukite AH, Corey JE. Metal movement in sludge amended soils: A nine year study. *Soil Sci.* 1987;14:124–131.
16. Chang AC, Page AL, Warneke JE, Grgurevic E. Sequential extraction of soil heavy metals following a sludge application. *J Environ Qual.* 1984;13:33–38.
17. Sims JT, Une JS. Chemical fractionation and plant uptake of heavy metals in soils amended with CO-composted sewage sludge. *Environ. Qual.* 1991;20:387–395.
18. Taylor RW, Xiu H, Mehadi AA, Shuford JW, Tadesse W. Fractionation of residual cadmium, copper, nickel, lead, and zinc in previously sludge-amended soil. *Comm. Soil Sci. Plant Anal.* 1995;26:2193–2204.
19. Swami D, Buddhi D. Removal of contaminants from Industrial wastewater through various non-conventional technologies: A review. *Int. J. Environ. Pollut.* 2006;27(4):324–346.
20. Inbaraj BS, Sulochana N. Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa*. *J Hazard Mat.* 2006;133 (1-3):283–290.
21. Rowell DL. Soil science: Method and application, Longmangrop, p. 345 Limitation Score, Computers & Geosciences; 1994.
22. Alyüz B, Veli S. Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *J. Hazard. M.* 2009;167:482–488.
23. Terzano R, Spagnuolo M, Medici L, Dorriné W, Janssens KCP. Ruggiero microscopic single particle characterization

- of zeolites synthesized in a soil polluted by copper or cadmium and treated with coal fly ash. *Appl. Clay Sci.* 2007;35:128–138.
24. Rauret G, López-Sánchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, Quevauviller P. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* 1999;1:57–61.
 25. Salbu B, Kjekling T, Oughton DH. Characterization of radioactive particles in the environment. *Analyst.* 1998;123:843–849.
 26. Zafar SI, Bisma M, Saeed A, Qqbal M. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, and SEM-EDX analysis for describing mechanism of biosorption of the cationic basic dye methylene blue by a new biosorbent (sawdust of silver fir; *Abies pindrow*), Fresen. *Bull. Environ. Contam. Toxic.* 2008;17:2109–2121.
 27. Saeed A, Iqbal M, Zafar SI. Immobilization of *Trichoderma viride* for enhanced methylene blue biosorption: batch and column studies. *J. Hazard. Mater.* 2009;168:406–415.
 28. Iqbal M, Saeed A. Biosorption of reactive dye by loofa sponge-immobilized fungal biomass of *Phanerochaete chrysosporium*, *Process Biochem.* 2007;42:1160–1164.
 29. Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Analyt. Chem.* 1979;51:844–851.
 30. Ho YS. Effect of pH on lead removal from water using tree fern as the sorbent. *Bioresour. Technol.* 2005;96:1292–1296.
 31. Garau G, Castaldi P, Santona L, Deiana P, Melis P. Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. *Geoderma.* 2007;142:47–57.
 32. Komisarek J, Wiatrowska K. Effectiveness of oxide-amendments in the stabilization process of Cu, Pb and Zn in Artificially Contaminated Soil. *Polish J. Environ. Studies* 2009;18(6):1029–1038.
 33. Manahan SE. *Environmental science and technology.* New York: Lewis; 1997.
 34. Narwal RP, Singh BR, Salbu B. Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions. *Comm. Soil Sci. Plant Anal.* 1999;30:1209–1230.
 35. Ahumada I, Mendoza J, Ascar L. Sequential extraction of heavy metals in soils irrigated with wastewater. *Commun. Soil Sci. Plant Anal.* 1999;30:1507–1519.
 36. Luo XS, Zhou DM, Liu XH, Wang YJ. Solid/solution partitioning and speciation of heavy metals in contaminated agricultural soils around a copper mine in eastern Nanjing city, China. *J. Hazard. Mater.* 2006;131:19–27.
 37. Rieuwerts JS, Thornton I, Farago ME, Ashmore MR. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chem. Spec. Bioavail.* 1998;10:61–75.
 38. McLean JE, Bledsoe BE. *Ground Water Issue Behavior of Metals in Soils.* EPA; 1992.
 39. Sayed SA, Zayed AM. Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups. *Desalination.* 2006;194(1-3):90–100.
 40. Wilson K, Yang H, Seo CW, Marshall WE. Select metal adsorption by activated carbon made from peanut shells. *Bioresour. Technol.* 2006;97(18):2266–2270.
 41. Fitzmorris KB, Lima IM, Marshall WE, Reimers RS. Anion and Cation Leaching or desorption from activated carbons from municipal sludge and poultry manure as affected by pH. *Water Environ. Res.* 2006;78(12):2324–2329.

© 2015 Lorestani et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:

<http://www.sciencedomain.org/review-history.php?id=795&id=32&aid=6891>