Stabilization of nickel in a contaminated calcareous soil amended with low-cost amendments

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Abstract

A laboratory study was planned to delineate the benefits of some low-cost soil amendments on Nickel (Ni) stabilization in a Ni-spiked soil. Six different kinds of amendments were evaluated by desorption kinetic test and sequential extraction procedure to determine their ability to reduce mobility of Ni in a Ni-spiked soil. The Ni-spiked soil was separately incubated with coal fly ash (CFA), rice husk biochars prepared at 300°C (B300) and 600°C (B600), municipal solid waste compost (MSWC), zero valent iron (Fe⁰) and zero valent manganese (Mn⁰) at 2 and 5% (W/W) for 45 and 90 days at 25 °C. The kinetic data obtained from 0.01 M EDTA was used to simulate desorption equations. The Sequential extraction method was also used as a suitable method for identification of chemical forms of Ni and its mobility. According to the results, application of amendments reduced exchangeable and carbonate forms of Ni with respect to control treatment. Changes in chemical forms of Ni and their conversion into less soluble forms in treated soils was observed with incubation time. Application of Mn⁰, Fe⁰, CFA, and B300 to soil samples significantly decreased Ni desorption rate compared to the control treatment. The lowest Ni release was achieved by Mn⁰-treatment at 5%. Biphasic pattern of Ni desorption kinetic was fitted well by the model of two first-order reactions. From the practical point of view, Fe⁰, Mn⁰, CFA, and B300 treatments are effective in Ni stabilization, while using Mn⁰ and Fe⁰ at 5% can be recommended for immobilization of Ni from calcareous polluted soil.

Keywords: Nickel, amendments, stabilization, chemical forms, desorption kinetic

1. Introduction

Soil contamination by heavy metals, specially derived from anthropogenic sources, due to their toxicity effect on human health, has been known as a serious environmental problem for last few decades. Nickel (Ni) is one of the heavy metals, which its concentration significantly increases nowadays

due to industrial development (Ramachandran and D'Souza, 2013). In addition, some sewage sludges and phosphate fertilizers may be important sources of Ni in agricultural soils (Kabata-Pendias and Mukherjee, 2007). Clay content, Fe and Mn-Oxides, and pH are the most important factors affecting the mobility of Ni in soils. Leaching down of Ni to the

groundwater often occur in acidic condition with maximum ionic $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ concentration, however at alkaline condition, Ni may precipitate as hydroxides such as $\text{Ni}(\text{OH})_3$ or $\text{Ni}_4(\text{OH})_4^{4+}$, with low solubility (Alloway, 2013). Nickel in soils is slightly mobile and associated with residual fraction (Kabata-Pendias and Mukherjee, 2007). The stabilization of heavy metals-contaminated soils using contaminant-immobilizing amendments is a remediation procedure practical to decrease element dynamic in soils (Zhao *et al.*, 2014). Stabilization of pollutants in soil can be achieved by adsorbing, complexing or precipitating of heavy metals. Heavy metals mobility is controlled by sorption and desorption characteristics of soil (Zhao *et al.*, 2014). The desorption rate constants of heavy metals in soils can be related to its mobility and toxicity (Violante *et al.*, 2008). In addition, the study of desorption kinetics can predict how the pollutants are transferred from the solid phase to the liquid phase (Jalali and Sajaditabar, 2013). Sequential extraction methods are applied to give qualitative and quantitative information about chemical forms of metals in soils (Jalali and Rostaei, 2011). However, fractionation of heavy metals by selective sequential extractions is practical, but previous studies showed that chemical extractants used in sequential extractions methods are not completely selective and specific (Saffari *et al.*, 2009), and readsorption and redistribution of metal ions after release can occur (Saffari *et al.*, 2009). In last decade, researchers have preferred to apply kinetic methodologies rather than the conventional sequential extraction techniques for evaluation of heavy metals behavior. Santos *et al.*, (2010) explained that dynamic of heavy metals depends not only on their distribution among several species, but also on the dynamic properties of those species, such as chemical rate constants and diffusion coefficients. Hence, methodologies involving the

kinetic fractionation of heavy metals in soils and sediments have been developed (Santos *et al.*, 2010; Jalali and SajadiTabar, 2013). Bioavailability of heavy metals in soil is directly impacted by residence time (Jalali and khanlari, 2008). Heavy metals have highest bioavailability immediately after application to soil and with increasing time, bioavailability of metals decreases (Jalali and khanlari, 2008;). There is no information on stabilization of Ni in calcareous soils. Therefore, the objective of present study were to investigate the influence of some amendments (coal fly ash, municipal solid waste compost, two types of biochar of rice husk prepared at 300 and 600°C, zero valent iron and zero valent manganese) and incubation times on release and chemical transformation of Ni in a Ni-spiked soil, and to compare the ability of these amendments to reduce the mobility of Ni in a contaminated soil via desorption kinetic and sequential extraction experiments.

2. Materials and Methods

2.1. Soil sampling and analysis

Soil sample was collected from the 0–30 cm depth of a calcareous soil (Fine, mixed, mesic, Fluventic Calcixerepts) from agricultural fields located in College of Agriculture, Bajgah, Shiraz, Fars Province, Iran. Soils was air-dried and passed through a 2 mm sieve. Soil texture, pH, electrical conductivity (ECe), percentage of calcium carbonate equivalent (CCE), cation exchange capacity (CEC), and organic matter (OM) determined using standard methods (Sparks *et al.*, 1996). Plant-available of heavy metals were extracted by DTPA and determined by atomic absorption spectrophotometer. Total contents of heavy metals were determined using 4M HNO_3 . The related properties of soil are presented in Table 1.

Table 1. Selected chemical and physical properties of studied soil.

Property	Value	Property	Value
pH	7.8	Soluble Fein DTPA(mg kg ⁻¹)	4.1
CCE (%)	39.5	Soluble Cuin DTPA(mg kg ⁻¹)	0.92
Sand (%)	27	Soluble Mn in DTPA(mg kg ⁻¹)	5.6
Clay (%)	35	Soluble Pb in DTPA(mg kg ⁻¹)	Trace
OM (%)	1.4	Soluble Ni in DTPA(mg kg ⁻¹)	Trace
CEC (Cmol(+) kg ⁻¹)	15.8	Total Ni (mg kg ⁻¹)	51
EC (dS m ⁻¹)	0.65	Total Fe (mg kg ⁻¹)	30554

Table 2. Summary of the Sequential extraction procedure used in this study

g soil:mL solution	Extracting solution	Shaking time (h)	Chemical form of Ni	Symbol
10:40	1 M Mg(NO ₃) ₂	2	Exchangeable	EX
10:40	1M NaOAc (pH=5 CH ₃ COOH)	5	Carbonate- bound	Car
10:20	0.7M NaOCl (pH=8.5)	0.5 in boiling water bath	Organically- bound*	Om
5:50	0.1M NH ₂ OH.HCl (pH=2 HNO ₃)	0.5 in boiling water bath	Mn-oxide- bound	Mn-OX
5:50	0.25M NH ₂ OH.HCl+ 0.25M HCl	0.5 at 50 °C in water bath	Amorphous Fe-oxide-bound	FeA-Ox
5:50	0.2M (NH ₄) ₂ C ₂ O ₄ +0.2M H ₂ C ₂ O ₄ +0.1 MC ₆ H ₈ O ₆	0.5 in boiling water bath	Crystalline Fe- oxide-bound	FeC-Ox

*Two times extraction

Table 3. Equations fitted to describe Ni release kinetic

Model	Equation	Parameters
Zero order	$q_t = q_0 - k_0 t$	K_0 , zero order rate constant (mg Ni kg ⁻¹ h ⁻¹)
First order	$\ln q_t = \ln q_0 - k_1 t$	k_1 , first-order rate constant (h ⁻¹)
Second order	$1/q_t = 1/q_0 - k_2 t$	k_2 , second-order rate constant [(mg Ni kg ⁻¹) ⁻¹]
Third order	$t/q_t^2 = 1/q_0^2 - k_3 t$	k_3 , third-order rate constant[(mg Ni kg ⁻¹) ⁻² h ⁻²]
Parabolic diffusion	$q_t = q_0 - k_p t^{1/2}$	k_p , diffusion rate constant [(mg Ni g ⁻¹) ^{-0.5}]
Simple Elovich	$q_t = 1/\beta \ln(\alpha_s \beta_s) + (1/\beta_s) \ln t$	α_s , initial desorption rate (mg Ni kg ⁻¹ h ⁻¹), β_s desorption constant [(mg Ni kg ⁻¹) ⁻¹]
Two-constant rate	$q_t = at^b$	a , initial desorption rate constant (mg Ni kg ⁻¹ h ⁻¹) ^b b , desorption rate coefficient [(mg Ni kg ⁻¹) ⁻¹]

 q_0 and q_t are the amount of Ni desorption (mg kg⁻¹) at time zero and t, respectively.

Table 4. Values of seven equations and a model in examined soils after 45 days of incubation time

Equation	Value	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Control
Zero order	R ²	0.57	0.5	0.51	0.44	0.4	0.39	0.38	0.4	0.37	0.44	0.37	0.4	0.39
	SE	3.42	3.36	3.48	3.71	3.48	3.77	3.74	3.68	3.41	3.56	4.1	3.74	3.9
First order	R ²	0.32	0.29	0.29	0.24	0.23	0.23	0.22	0.23	0.21	0.23	0.21	0.22	0.23
	SE	4.62	4.35	5.45	3.32	3.73	3.34	4.32	4.45	4.8	4.28	4.34	4.01	4.1
Second order	R ²	0.09	0.1	0.08	0.07	0.08	0.09	0.08	0.07	0.08	0.07	0.07	0.07	0.09
	SE	7.66	6.99	7.87	7.92	7.63	7.8	7.62	7.54	7.63	7.65	7.91	7.82	7.26
Third order	R ²	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.04
	SE	9.35	8.44	10.41	7.05	7.65	6.77	8.26	6.81	6.83	7.5	7.33	5.97	7.38
Parabolic diffusion	R ²	0.81	0.75	0.75	0.67	0.63	0.63	0.61	0.63	0.59	0.66	0.6	0.64	0.62
	SE	2.38	2.37	2.85	2.07	2.42	2.16	2.72	2.13	2.21	2.19	2.37	1.83	2.37
Simple Elovich	αs	26.2	22.31	23.26	35.69	52.92	54.18	74.21	26.31	67.81	52.58	23.29	17.6	93.58
	βs	0.62	0.68	0.56	0.9	0.81	0.91	0.74	0.92	0.94	0.85	0.86	1.05	0.84
	R ²	0.98	0.99	0.99	0.98	0.98	0.97	0.97	0.97	0.97	0.99	0.97	0.98	0.98
	SE	0.61	0.51	0.52	0.57	0.54	0.51	0.67	0.59	0.59	0.43	0.64	0.48	0.56
Two-constant rate	a	3.88	3.33	3.74	3.1	3.84	3.57	4.43	2.67	3.6	3.64	2.56	2.08	4.44
	b	0.22	0.23	0.24	0.21	0.2	0.19	0.2	0.23	0.19	0.2	0.25	0.25	0.18
	R ²	0.89	0.9	0.89	0.82	0.86	0.84	0.82	0.84	0.8	0.81	0.83	0.83	0.83
	SE	1.52	1.8	2.3	1.7	1.93	1.68	2.24	1.95	1.84	1.8	2.38	1.8	1.76
two first-order reactions	Q ₁	8.975	7.964	9.528	5.62	6.872	6.282	7.288	5.489	5.423	5.840	5.511	4.67	8.96
	K ₁	0.006	0.009	0.008	0.018	0.026	0.028	0.028	0.022	0.028	0.016	0.021	0.016	0.016
	Q ₂	6.877	6.009	7.486	5.331	5.490	4.824	6.465	4.780	5.515	6.124	5.256	4.23	4.23
	K ₂	1.326	1.011	0.808	1.242	2.049	2.592	2.008	0.997	1.687	1.466	0.7196	0.805	0.80
	R ²	0.98	0.97	0.98	0.97	0.98	0.98	0.98	0.97	0.98	0.98	0.98	0.98	0.98
	SE	0.6	0.48	0.51	0.53	0.54	0.54	0.58	0.55	0.58	0.52	0.66	0.49	0.53
	Q ₁ /Q ₂	1.143	1.325	1.273	1.056	1.25	1.302	1.127	1.148	0.983	0.954	1.049	1.104	2.11

Table 5. Values of seven equations and a model in examined soils after 90 days of incubation time

Equation	Value	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Control
Zero order	R ²	0.31	0.3	0.33	0.38	0.22	0.31	0.34	0.31	0.3	0.31	0.28	0.32	0.34
	SE	3.01	2.84	3.21	2.57	3.43	3.21	3.45	3.22	3.7	3.27	3.47	3.22	3.17
First order	R ²	0.14	0.15	0.16	0.16	0.11	0.14	0.16	0.16	0.14	0.15	0.14	0.16	0.17
	SE	6.9	7.1	6.83	6.81	7.42	6.51	6.43	6.12	6.33	6.38	6.51	5.98	6.13
Second order	R ²	0.03	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.06
	SE	7.44	7.1	7.22	7.432	7.74	7.1	7.22	7.41	7.74	7.34	7.54	7.62	7.43
Third order	R ²	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03
	SE	6.74	6.87	6.3	6.45	6.02	6.9	6.3	6.35	6.71	6.63	6.23	6.28	6.15
Parabolic diffusion	R ²	0.52	0.51	0.55	0.6	0.41	0.52	0.56	0.53	0.51	0.53	0.49	0.55	0.57
	SE	2.28	2.37	2.85	2.07	2.48	2.31	2.08	2.13	2.21	2.19	2.37	1.83	2.37
Simple Elovich	αs	27.5	36.1	35.5	25.3	53.13	30.99	23.96	17.71	39.3	29.7	30.91	10.28	26.26
	βs	0.99	0.97	1.11	1.1	1.15	0.88	1.09	0.84	1.12	1.08	1.21	1.27	0.87
	R ²	0.95	0.94	0.96	0.98	0.89	0.95	0.96	0.94	0.95	0.96	0.94	0.95	0.97
	SE	0.7	0.76	0.53	0.39	0.95	0.74	0.73	0.68	0.87	0.63	0.71	0.69	0.51
Two-constant rate	a	2.18	2.56	2.39	2.13	2.38	2.43	2.07	2	2.37	2.2	2.09	1.29	2.58
	b	0.27	0.25	0.24	0.25	0.24	0.27	0.26	0.3	0.24	0.25	0.24	0.3	0.25
	R ²	0.73	0.75	0.75	0.75	0.68	0.73	0.77	0.78	0.73	0.74	0.75	0.8	0.8
	SE	1.52	1.8	2.31	1.97	2.22	1.62	1.57	1.82	1.9	1.87	1.58	1.8	1.76
two first-order reactions	Q ₁	3.73	3.84	3.6	3.96	3.15	4.05	3.48	3.57	3.2	3.59	3.58	3.28	5.92
	K ₁	0.01	0.02	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.74
	Q ₂	5.85	6.09	5.35	5.05	5.41	6.88	5.27	7.17	5.65	5.46	4.42	3.68	5.02
	K ₂	0.61	0.68	0.85	0.82	0.83	0.6	0.62	0.3	0.76	0.72	0.98	0.43	0.01
	R ²	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.99	0.99	0.99	0.99	0.99
	SE	0.26	0.31	0.27	0.31	0.32	0.32	0.34	0.39	0.25	0.36	0.31	0.25	0.28
	Q ₁ /Q ₂	0.637	0.63	0.673	0.784	0.583	0.589	0.661	0.499	0.567	0.657	0.808	0.892	1.18

Table 6. Simple correlation coefficient (r) between parameters of two first-order reactions, Elovich equation and chemical forms of Ni in amended soils after 45 (Below the diagonal, white background) and 90 (Above the diagonal, gray background) days of incubation time.

	Q ₁	K ₁	Q ₂	K ₂	as	βs	EX	Car	Om	Mn-Ox	FeA-Ox	FeC-Ox	Res
Q ₁	1	0.913 ^{***}	0.016	-0.664 ^{***}	-0.17	-0.582 ^{**}	0.48	0.421	0.023	0.105	0.104	0.305	-0.413
K ₁	-0.507	1	-0.164	-0.711 ^{***}	-0.078	-0.396	0.371	0.483	-0.021	0.102	0.212	0.38	-0.463
Q ₂	0.562	-0.408	1	-0.141	0.193	-0.802 ^{***}	0.607 [*]	-0.406	0.727 ^{***}	-0.499	-0.169	-0.301	0.499
K ₂	-0.123	0.720 ^{***}	0.056	1	0.527	0.601	-0.286	-0.043	-0.393	-0.164	-0.205	-0.255	0.309
as	0.155	0.610 [*]	-0.208	0.441	1	0.082	0.404 ^{**}	0.213	-0.046	-0.466	-0.107	-0.226	0.246
βs	-0.871 ^{***}	0.571	-0.857 ^{***}	0.087	0.13	1	-0.741	0.115	-0.678 ^{***}	0.258	0.078	0.086	-0.11
EX	0.546 [*]	-0.054	-0.12	0.171	0.403	-0.302	1	0.263	0.611 [*]	-0.212	-0.289	-0.371	-0.07
Car	0.409	-0.357	-0.08	-0.45	-0.061	-0.235	0.345	1	-0.198	0.446	-0.311	0.018	-0.809 ^{***}
Om	0.254	-0.071	0.022	0.222	-0.026	-0.249	0.694 ^{***}	-0.122	1	-0.037	-0.408	-0.289	0.053
Mn-Ox	-0.128	-0.103	-0.35	-0.344	-0.344	0.215	-0.109	0.447	-0.084	1	-0.564 ^{**}	0.31	-0.854 ^{***}
FeA-Ox	-0.166	-0.087	-0.071	-0.292	0.174	0.252	-0.404	-0.282	-0.589 [*]	-0.397	1	-0.009	0.431
FeC-Ox	-0.041	-0.207	0.44	0.039	-0.401	-0.207	-0.444	-0.32	-0.246	-0.52	0.323	1	-0.245
Res	-0.381	0.374	0.206	0.483	0.108	0.165	-0.429	-0.951 ^{***}	-0.047	-0.619	0.361	0.48	1

2.2. Additive samples and incubation experiment

Six different amendments including coal fly ash (CFA), municipal solid waste compost (MSWC), rice husk biochars prepared at 300°C (B300) and 600°C (B600), zero valent iron (Fe⁰) and zero valent manganese (Mn⁰) were used in present study. CFA and MSWC were collected from Zarand coal washing factory and recycling and municipal solid waste compost factory of Kerman, Iran, respectively. CFA contained 46.47% of SiO₂, 27.32% of Al₂O₃, 0.9% of TiO₂, 6.73% of Fe₂O₃, 4.56% of CaO, 0.15% of BaO, 0.14% of SrO, 2.32% of MgO, 3.42% of K₂O, 0.82% of Na₂O, 4.6% of SO₃, 4.6% of P₂O₅, and 0.82% of Mn₃O₄, and its pH value was 9.1. MSWC had 38% organic matter, and contained 19 mgkg⁻¹ of Cu, 28mgkg⁻¹ of Zn, 25 mgkg⁻¹ of Fe, 11 mgkg⁻¹ Mn, 13.3 mgkg⁻¹ Pb, 0.28 mgkg⁻¹ Cd, and 1.2 mgkg⁻¹ of Ni, and its pH and EC values were 7.4 and 19.36, respectively. Biochars were prepared at 300°C and 600°C from rice husk. Husk samples (covered with aluminum foil) were placed in a furnace for 4h to produce biochars.

Zero valent iron grit (Fe⁰, 99.5%) and zero valent manganese grit (Mn⁰, 99.5%) were used in present study. The concentrations of carbon, hydrogen and nitrogen in biochars samples were determined with CHN analyzer. The elemental content of C, H, and N in B300 sample was 41.57, 2.11, and 1.52% respectively. Its pH and EC values were 6.2 and 13.1, respectively. In contrast, the average elemental composition of B600 was 48.99% C, 1.55% H, and the percentage of N was trace. Its pH and EC values were 8.7 and 21.2, respectively. In addition, Fourier Transform Infrared Spectroscopy (PerkinElmer FT-IR: Spectrum RX1) was used for the recognition of the morphology and structure of the produced biochars (Figure 1). For incubation study, soil samples were placed in plastic cups and Ni was added at rate of 250µg g⁻¹ as Ni(NO₃)₂. Selected amendments including CFA, MSWC, biochars of rice husk (B300 and B600), Fe⁰, and Mn⁰ were added to each soil sample separately, at two levels (2 and 5% W/W). The soil samples were incubated for 45 and 90 days at 25°C. The moisture was kept at about field capacity (FC) by adding distilled

water to a constant weight. After incubation times, samples were air-dried and used for Ni desorption and fractionation studies. The description of experimental treatments is as; S1 and S2 (MSWCat 2 and 5 %), S3 and S4 (CFAat 2 and 5 %), S5 and S6 (B300 at 2 and 5

%), S7 and S8 (B600at 2 and 5 %), S9 and S10 (Fe⁰at 2 and 5 %), S11 and S12 (Mn⁰ at 2 and 5%). A control treatment (Control) with no amendment addition was also prepared. Each treatment was carried out in triplicates.

Figure1. FTIR spectra of rice husk before pyrolysis (B0), and after pyrolysis (B300 and B600).

2.3. Sequential extraction procedures

Chemical distribution of Ni in soil was determined using Singh *et al.*, (1988) method. The procedure was designed to separate Ni into seven fractions. Residual form (Res) is calculated by subtracting sum of six fractions from total Ni. Outline of the method is presented in Table 2. Also, the mobility of Ni was assessed by a “mobility factor” which calculated according to the equation: $(EX + Car / \text{sum of fractions}) \times 100$.

2.4. Kinetics Studies

For Ni desorption studies, 5 g of air-dried was placed in polyethylene tubes and extracted with 25 ml of 0.01 M EDTA at pH 7.0. Samples were shaken for periods of 0.08 to 2000 h (0.08, 0.25, 0.58, 1.25, 2.25, 4.25, 8.25, 16.25, 30.25, 54.25, 102.25, 150, 300, 450, 700, 1000, 1400, and 2000 h) at $25 \pm 2^\circ\text{C}$ and then centrifuged immediately at 2500 rpm. The samples were filtered through Whatman 42 filter paper and Ni concentration was determined using atomic absorption spectrophotometer (Shimadzu AA-670G). Different kinetic equations were used to describe desorption of Ni in soils (Table 3).

Figure 2. Relative distribution of chemical forms of Ni in amended soils after A) 45 and B) 90 days of incubation time.

2.5. Model fitting to kinetic data

A two first-order reaction model can divide heavy metal into three fractions (Santos *et al.*, 2010; Jalali and Sajadi Tabar, 2013), Q_1 , Q_2 and Q_3 , where:

$$q = Q_1 (1 - e^{-k_1 t}) + Q_2 (1 - e^{-k_2 t})$$

$$Q_3 = q_{total} - Q_2 - Q_1$$

q represents amount of metal released at time t .

Q_1 (mg kg^{-1}): “labile” fraction, readily extractable, associated to the rate constant k_1 .

Q_2 (mg kg^{-1}): “moderately labile” fraction, less extractable, associated to the rate constant k_2 .

Q_3 (mg kg^{-1}): Ni fraction, which is not extractable

q_{total} : total concentration of Ni in soil.

To determine the best-fitted model, a standard error of estimate was calculated for each equation and model. A relatively high values of coefficients of determination (R^2) and low values of standard errors of estimate (SE) were used as criteria for the selection of the best-fitted models. The standard error was calculated as follows:

$$SE = \left[\frac{\sum (E - E')^2}{n - 2} \right]^{0.5}$$

Where E and E' are the measured and calculated amounts of Ni release in soil at time t, respectively, and n is the number of measurements.

2.6. Statistical analysis

The regression of linear, nonlinear procedure and other statistical analyses were calculated by Microsoft Excel 2010 and SPSS V19.

Figure 3ab. Cumulative released Ni with time in treated soils after 45 days of incubation time

Figure 3cd. Cumulative released Ni with time in treated soils after 90 days of incubation time

Fig. 4. Experimental ($\diamond$) and predicted values ($\blacksquare$) of Ni desorption in six amended soils after 45 days' incubation—predicted by simple Elovich equation.

Fig. 5. Experimental (♦) and predicted values (■) of Ni desorption in six amended soils after 45 days' incubation—predicted by two first-order reaction model.

3. Result and Discussion

3.1. Characterization of Biochars amendments

According to the results of biochars analysis, elimination of unstable compounds at the higher temperatures caused biochars to have higher percentages of carbon (C), while much lower hydrogen (H) and nitrogen (N) contents. Increased pyrolysis temperature led to increased pH (from 6.2 to 8.7) and EC (from 13.1 to 21.2 dS m⁻¹). Figure 1 showed the FTIR spectra of rice husk before pyrolysis (B0), and after pyrolysis (B300 and B600). The sharp peak at 3405 and 3416 cm⁻¹ in B0 and B300, and the weak peaks at around 3585 cm⁻¹ in B300 and B600 are due to hydroxyl group (–OH) stretching and functional group of phenol. The peaks at 2923 and 2936 cm⁻¹ seen in B0 and B300 are ascribed to aliphatic C–H deforming vibration and functional group of alkanes. These functional groups disappear at temperatures higher than 600°C. The weak band at 1725 cm⁻¹ for B0, which disappear at temperatures higher than B300, is assigned to C=O stretching in carbonyl group and neutral functional group of aldehydes. The weak band at around 1640 cm⁻¹ for B0 is due to the presence of or C=C stretching (functional group of alkenes). The weak band 1539 cm⁻¹ for B0 indicates the presence of N–O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300°C indicating the volatilization of nitrogen forms. The band at around 1600 cm⁻¹ for B300 and B600 indicated the presence of aromatic C=O ring stretching (likely –COOH) or C=C stretching of aromatic. This band is stronger in B600 compared to B300, which for this reason; pH was higher than B300. The weak bands at 1320 cm⁻¹ and 1376 cm⁻¹ in B0 indicate the presence of the N–O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300°C, indicating the volatilization of nitrogen forms. The

band at around 1090 cm⁻¹ is due to aliphatic ether, alcohol C–O or aromatic stretching in cellulose and hemicelluloses. Generally, the results from FTIR analysis of B600 showed the functional groups such as carboxylic bonds and aromatic C=O ring stretching (likely –COOH) was higher than B300, which increased its pH.

3.2. Chemical forms of Ni affected by aging and amendments

Figures 2A and 2B show the relative distribution of Ni in seven fractions in amended soil samples, incubated for 45 and 90 days, respectively. The results showed that the distribution of chemical forms of Ni was affected by incubation times. Distribution of chemical forms of Ni in soil samples after 45 days' incubation followed the order: Res > Car > FeA-OX > Mn-OX > EX > Om > FeC-OX. On the other hand, after 90 days' incubation Ni fractions decreased in the following order: Res > FeA-OX > Car > Mn-OX > FeC-OX > Om > EX. With increasing time EX, Car and Om fractions decreased, but Mn-OX, FeA-OX, FeC-OX and Res fractions increased. Rajaie *et al.*, (2008) reported that incubation time had a significant effect on chemical forms of Ni. Their results showed that, added soluble Ni at the beginning of experiment was presented in mobile fractions (EX and Car forms), but with increasing time EX and Car fractions converted into oxides and Res forms with lower mobility. Increasing Ni bound to FeA-OX after 90 days' incubation, could be due to high sorption affinity of Ni for Fe oxides (Rajaie *et al.*, 2008). The change in chemical forms of heavy metals with time into less soluble forms reported by others (Jalali and Rostaie, 2011; Jalali and Khanlari, 2008). In soil samples, Ni was strongly bound with Res fraction, which was in agreement with other studies (Jalali and Sajadi Tabar, 2013; Rajaie *et al.*, 2008). Significant reductions in

EX form were observed in treated soil. The highest decrease in this fraction was observed following the application of $\text{Mn}^0_{5\%}$. EX form is an available fraction, which demonstrated application of amendments decreased Ni availability in soil samples. In addition, a considerable reduction of Car form following the soil treatment was observed. Nearly 57 and 70.26% of Car bound to Ni was decreased by $\text{Fe}^0_{5\%}$ in treated soil after 45 and 90 days' incubation compared to the control, respectively. Om fraction decreased after adding the CFA, Mn^0 , and Fe^0 . In contrast, application of organic amendments (B300, B600 and MSWC) increased Om fraction. The highest decreasing and increasing amount of Om fraction followed by addition of $\text{CFA}_{5\%}$ and $\text{B600}_{5\%}$, respectively. Garcia-Delgado *et al.*, (2007) investigated the effect of sewage sludge on chemical forms of heavy metals. They showed that adding sewage sludge increased Cd concentration in EX and Om fractions, but did not affect of Ni fractionation. McGrath and Cegarra (1992) studied the impact of 20 years application of sludge on chemical forms of Ni. They reported that after 10 years application of sludge, Ni in the Car, OM, and EX fractions increased, and the percentage of the Res fraction decreased with time. However, after 20 years application of sludge, EX, OM, and Car fractions declined slightly, and the Res fraction increased with time. The change in Ni bound to Mn-OX following the application of Mn^0 and Fe^0 was more evident. Application of Mn^0 increased Mn-OX, but addition of Fe^0 decreased Mn-OX fraction. Chemical forms of FeA-OX and FeC-Ox did not change in treated soils. In control soil, the mobility factor was 35.17% and 28.09% for 45 and 90 days' incubation, respectively. In soil samples, the lowest mobility factor was associated with $\text{Fe}^0_{5\%}$. The mobility factors in S1-S12 respected to the control treatment were 27.79, 30.10, 25.15, 24.32, 25.08, 21.58, 20.27, 18.02, 25.15, 14.69, 29.04, and 24.29%, respectively, in 45 days'

incubation. In contrast, increasing incubation time from 45 to 90 days decreased mobility factor of Ni. The mobility factors in S1-S12 compared to the control were 16.68, 17.87, 15.05, 14.54, 15.43, 13.11, 12.68, 10.77, 15.17, 8.98, 17.27, and 14.13%, respectively in 90 days of incubation time. Addition of amendments generally led to a significant reduction in mobility of Ni in both of incubation times.

3.3. Release of Ni affected by amendments

Figure 3ab show the trend of Ni desorption in soil samples under different amendments and incubation times. The results showed that there was a similar pattern of initial rapid release followed by slower release of Ni with time, however the rate of Ni desorbed after 45 days' incubation was higher than 90 days' incubation. This could be due to the higher adsorption of Ni with time. Depending on the metal and sorbent, residence time can affect the quantity of desorption of heavy metal (Jalali and Sajadi Tabar, 2013). Heavy metals have highest bioavailability immediately after application to soil (Jalali and Rostaei, 2011, Rajaie *et al.*, 2008). Ainsworth *et al.*, (1994) studied the effect of residence time on Pb^{2+} and Co^{2+} desorption from hydrous Fe oxide. They reported that residence time had significant effect on the amount of Pb and Co desorbed, which could be ascribed to the strong metal-soil complexes that occur and perhaps to diffusion processes. McNear *et al.*, (2007) explained that, at high solution Ni concentrations and pH values > 6.8 , Ni-Al LDH precipitates (formation of Ni and Al layered double hydroxide) can lead to a reduction in Ni mobility with time. In comparison with the non-amended soil, Mn^0 and Fe^0 caused a reduction in Ni release, ranging from 4% to 30% for 45 days' incubation. The highest reduction in Ni release occurred following addition of Mn^0 at 5%. Moreover, compared to the control, addition of Mn^0 or Fe^0

significantly decreased Ni release by 17% to 36% for $\text{Mn}^0_{5\%}$ and $\text{Fe}^0_{5\%}$, respectively for 90 days' incubation. Ni solution could be adsorbed to any of the surfaces soil solid phases, including layered silicates, $\text{Fe}(\text{Al})$ and Mn-OXides and organic substances (Arai, 2008). Fe and Mn-Oxides and hydroxides have an important role in retention, mobility and bioavailability of metals in contaminated soils (Kumpiene *et al.*, 2008). Increasing iron oxides decreased heavy metals mobilization (Friesl *et al.*, 2006, Kumpiene *et al.*, 2008,). Kumpiene *et al.*, (2006) applied 1% Fe^0 to reduce the mobility of Cr, Cu, As and Zn in a contaminated soil and showed that As and Cr concentrations decreased in soil leachates by 98% and 45%, respectively. Friesl *et al.*, (2003) showed that, application of red mud (as a soil amendment containing Fe oxides) decreased the mobility of Zn, Cd, and Ni in soils. By addition of MSWC at 2 and 5%, the release of Ni significantly increased compared to the control soil in 45 days' incubation. It seems that, MSWC caused produce soluble complexes with Ni and increased Ni release in 45 days' incubation. In contrast, 90 days' incubation with MSWC at these rates led to a significant reduction of Ni release in a range of 7%–10% at 90 days' incubation. Arnesen and Singh (1999) reported that extractable Cu increased with increasing rate of peat, and suggested that lowering pH in peat-amended soil probably decreased the sorption of Cu in soils. Among the Ni desorption process, addition of CFA decreased Ni release compared to the control (Except for $\text{CFA}_{2\%}$ in 45 days' incubation). Addition of 2 and 5% CFA decreased Ni release by 16% at the end of experiment. Application of CFA decreased efficiently mobility of soil heavy metals (Kumpiene *et al.*, 2008). Reduction of heavy metal mobility by CFA is due to two mechanisms: Increasing pH and specific surface area, which causes the precipitation of insoluble phases and promoting metal sorption via surface complexation. Soil samples

treated B600 at 2 and 5% decreased Ni release by 18% and 2.0% in of 90 days' incubation, respectively, but after 45 days' incubation, Ni desorption increased at 2%. Addition of B300 at 2 and 5% level decreased Ni release in both of incubation times (45 and 90 days). Application of B300 decreased Ni desorption by 2–20% in both incubation times. Depending on the temperature, biochars have different properties. Production of biochar at high temperature often produced biochar with highly aromatic substances, which recalcitrant to breakdown, high adsorptivity for heavy metals, high surface area, and high pH (Ladygina and Rineau, 2013). In contrast, biochars produced at low temperature often have high concentration of oxygenated functional groups, low pH, and high radical content and able to chemisorb oxygen (Ladygina and Rineau, 2013). Biochars produced at low temperature, adsorption capacity of heavy metals is variable (depends on type of biochar and soil). The results from FTIR analysis of B600 showed the functional groups such as carboxylic bonds and aromatic C=O ring stretching (likely –COOH) was higher than B300, which increased its pH. It was expected that, biochars (especially produced at high temperature) could reduce Ni release considerable. Due To the fact that used soil in present study is calcareous, it seems that higher calcium carbonate content (41%), probably was the main reason that biochar application could not efficiently affect immobilization of Ni. Among the amendments evaluated, application of Mn^0 resulted in the highest reduction Ni desorption in both of incubation times.

3.4. Equations and model fitting to kinetics of Ni desorption

The trends in cumulative Ni release in soil samples were similar. Initial rate of Ni desorption was fast but declined until reached equilibrium

(Figure 3cd). Desorption of Ni in all soil samples showed that 50% of total Ni desorbed within 16.25 h. Kirpichtchikova *et al.*, (2006) concluded that initial fast release of heavy metals from soil can be related to water-soluble fraction and adsorption sites with lower bonding energy. On the other hand, slower desorption of metals depend on less mobile forms and to the dissolution of mineral constituents of soil (Polettini *et al.*, 2007). Biphasic pattern of heavy metals desorption was observed by other (Sadeh *et al.*, 2012; Jalali and Sajadi Tabar, 2013). The zero order, first order, second order, third order, parabolic diffusion, simple Elovich and Two-constant rate equations were used for describing Ni release kinetics up to 2000 h (Table 4 and 5). The zero order, first order, second order, and third order equations could not be described Ni desorption kinetic in soil samples. Desorption of Ni affected by many soil factors, hence, it was clear that release patterns of Ni could not be described by a simple rate equations. However, Ghasemifasaei *et al.*, (2013) studied kinetics of Ni desorption from calcareous soils and reported that power function, first order, and second order equations were the best-fitted equations used to describe Ni desorption. Increasing order of reaction from zero to third caused the R^2 decreased in soils studied, which reported by Sadeh *et al.* (2012). Amount of R^2 and SE in the Tables 4 and 5 showed that best-fitted model for describing Ni release was simple Elovich equation. The Elovich equation is based on the assumption that the active surfaces of the sorbent are heterogeneous and therefore show different activation energies for chemisorption (Gupta and Babu, 2006). The higher fitness of the Elovich equation suggested that Ni sorption occur on heterogeneous surfaces of soil and the probably the mechanism is chemisorption. Witek-Krowiak *et al.*, (2011) clarified that α value in Elovich equation is the rate of chemisorption at zero coverage and β value is related to the extent of surface coverage and activation energy for adsorption.

Figure 4 shows the experimental extraction rate data and the fitted curves obtained with the simple Elovich equation for some amended soils. There was a good correlation between the fitted and experimental results for soil samples. Chien and Clayton (1980) concluded that the rate of Cu release increased when the value of α increased or β decreased in simple Elovich equation. Application of amendments decreased the values of α constant but the values of β constants increased compared to the control treatment in 45 days' incubation. Nevertheless, the trend was not true for 90 days' incubation. Therefore, additions of amendments were effective in immobilizing Ni in 45 and not in 90 days' incubation. With increasing incubation time, α and β did not change compared to the control soil. Addition of amendments decreased the values of 'a' constant (in the two constant equation) more than control soil in 45 and 90 days' incubation. Kuo and Mikkelsen (1980) reported that increased in value of 'a' probably increased rate of zinc desorption from soils. This is in agreement with the assumptions made about the role of amendments in reduction Ni desorption. The model of two first-order reactions were used by several researches (Santos *et al.*, 2010; Jalali and Sajadi Tabar, 2013). This model could be used as a kinetic methodology for metal speciation in soils and sediments. The model of two first-order reaction exhibited biphasic reaction: rapidly extracted followed by slowly extracted of metal. Hence, it was expected that this model could best be described Ni desorption. This model approach indicates the quantity and the extraction rate of metal fractions (Santos *et al.*, 2010). Tables 4 and 5 show that the parameters Q_1 , K_1 , Q_2 , K_2 , R^2 , SE, and Q_1/Q_2 . As results, R^2 was higher than 0.99 and values of SE were lower than SE obtained from Elovich equation, so this model was better than Elovich equation to describe kinetics of Ni desorption in soil samples. Figure 5 shows representative curves calculated from two first-

order reactions model. The results showed that, K_1 (coefficients of Ni for the rapid release phase) were higher than K_2 (coefficients of Ni for the slower release phase). The rate of Q_1 (quickly extracted) in amended soils was lower than control soil, meaning reduction Ni availability due to application amendments. High ratio of Q_1/Q_2 indicated that the labile metal fraction has greater than the less labile fraction. The lower ratio of Q_1/Q_2 of amended soils than control confirmed positive effect of amendment to stabilization of Ni. Application amendments increased the rate of Q_2 (slowly extracted) than control soil. This pattern was the same in both of incubation times. Brunori *et al.*, (2005) noticed that Q_1 could be related to EX fraction and part of Om fraction; Q_2 could be related to the Om residual and inorganic precipitates fraction, and Q_3 could be related to residual fraction. Simple correlation coefficients (r) was estimated for relationships among parameters of the two first-order reactions model, constants of Elovich equation, and chemical forms of Ni (Table 6). There was a positive significant between Q_1 with EX form, K_1 with α_s , K_1 with K_2 , Om, and EX in 45 days incubation time. In contrast, a negative significant correlation was found between Q_1 with β_s , Q_2 with β_s , Res with Car and Mn-OX fractions in 45 days incubation time. In 90 days' incubation time, there was a positive significant between Q_1 with K_1 , Q_2 with Om, EX with α_s . On the other hand, a negative significant correlation was found between Q_1 with K_2 , Q_1 with β_s , K_1 with K_2 , Q_2 with β_s , β_s with Om, and Res with Car and Mn-OX fractions in 90 days incubation time. Jalali and Sajadi Tabar (2013) reported that a significant correlation was found between Q_2 from acid malic with Om, inorganic precipitates fraction, and Res fractions. The results of correlation coefficient between Ni fractions and parameters of two first-order reactions and Elovich equation do not allow

any general conclusion, because the data are much different from the Brunori *et al.*, (2005) hypothesis.

4. Conclusions

In this study, the addition of coal fly ash, rice husk biochars prepared at 300°C and 600°C, municipal solid waste compost, zero valent iron and zero valent manganese have been evaluated for use in Ni-spiked soil. The addition of amendments to contaminated soil induced changes in Ni fractionation and desorption accordingly to the amendments properties. Zero valent iron and zero valent manganese decreased Ni desorption in soil, due to adsorption of Ni on surface of these amendments, which provides large surface area. Addition of coal fly ash changed the mobile fraction of Ni to less mobile in soils, which increased Ni stabilization, by increasing soil pH. Biochar prepared at 600 °C was an ineffective amendment for immobilizing Ni. It seems that high amount of calcium carbonate in studied soil probably was the main reason that biochar prepared at 600 °C could not efficiently affect immobilization of Ni. However, application of biochar prepared at 300 °C in soils significantly decreased Ni desorption rate, due to the increasing specific surface area that promoting Ni sorption through surface complexation. Different results obtained from application of municipal solid waste compost on Ni desorption did not allow any conclusion about positive effect of this amendment. In general, present study showed that from the practical point of view, all amendments (except for biochar prepared at 600°C and municipal solid waste compost) were effective in Ni immobilization, however application of zerovalent iron and zero valent manganese at 5% rate (W/W) were the best treatments to Ni immobilization. Further work is required to evaluate synergetic effects of selected amendments

on Ni stabilization, and it seems necessary to assess the relationship between Ni fractions as affected by selected amendment and plant uptake in calcareous contaminated soils.

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