

# An analytical deterministic model for simultaneous phyto remediation of Ni and Cd from contaminated soils

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**Abstract** Soil contamination by heavy metals, due to human activities, is not often limited to a single contaminant. The objective of this study was to develop a simple model for phytoextracting separate and combined Ni and Cd from contaminated soils. The study was further aimed to study phytoextraction potential of ornamental kale and land cress grown in soils contaminated with separate and combined Ni and Cd metals. The results indicated that elevated Ni and Cd concentrations in soil inhibit growth of both ornamental kale and land cress plants. In Ni+Cd treatments, growth and development of both plants were more affected than in either Ni or Cd treatments. Further, in Ni+Cd treatments, Ni concentration in tissues of both plants was increased by increasing soil Ni concentration under various Cd concentrations. At constant Ni concentration, addition of Cd did not appreciably change Ni content of plant tissues. Land cress demonstrated higher tolerance to soil contamination by Ni and Cd compared to ornamental kale. It also demonstrated higher phytoextraction potential for soil Cd than ornamental kale. Enhanced bioavailability of Ni and Cd ions, due to competitive adsorption and desorption reactions, had no reasonable effect on metal ion accumulation in plant tissues. This indicates that at relatively high soil contamination, metal ion adsorption is no longer a limiting factor for phyto remediation. The newly proposed model, which assumes that metal uptake rate inversely depends on total soil metal ion concentration, reasonably well predicted the cleanup

time of Ni, Cd, and Ni at the presence of Cd from the contaminated soils. The model also predicts that phyto remediation process takes much longer time when soil is contaminated by multi-metal ions.

**Keywords** Cadmium · Modeling · Nickel · Phytoextraction · Soil contamination

## Introduction

Both nickel (Ni) and cadmium (Cd) present in effluents of large number of industries. Soil contamination by Ni originates from silver refineries, electroplating, zinc-based casting and storage battery, mining, mineral and organic fertilizers, pesticides, and urban disposals (Ali et al. 2013; Wuana and Okieimen 2011). At very low concentrations, Ni is an essential element for some higher plants, which acts as a cofactor for the urease enzyme (Gheibi et al. 2009). It is also well known for its detrimental nature to plants and the environment when present in excess concentrations. The chronic toxicity of Ni to human health has been also recognized, such as gastrointestinal irritation, allergy, and cancer of lungs, nose, and bone (Ali et al. 2013). Cadmium does not have a known biological function in plants, and it is more phytotoxic than Ni (Atafar et al. 2010; Pålsson 1989). Sources of soil contamination by Cd are usually similar to those of Ni (Wei and Zhou 2006). Cadmium can reduce crop yields and influences animals and human health through the food chain (Jafarnejadi et al. 2013). In human, it induces some fatal diseases such as the “itai-itai disease” (Sun et al. 2009).

Due to the high costs, long-term disturbance of soil structure, and large scale of the contaminated areas, application of the current technologies such as leaching, solidification, vitrification, electrokinetic treatment, chemical oxidation or reduction,

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excavation and off-side treatment to remove metal ions from soil are not feasible options (Mulligan et al. 2001). Alternatively, phytoremediation can be used with much less limitations to remediate heavy metals from contaminated soils (Asadi Kapourchal et al. 2011). Among different types of phytoremediation, phytoextraction is the most efficient option in large-scale remediation projects, in which hyperaccumulator plants are used to extract and translocate heavy metals from the contaminated soil to their harvestable aboveground parts (Ali et al. 2013; Bert et al. 2009). A vital key in success or failure of any phytoextraction project is the time required to meet target metal concentration in the soil. Prediction of the cleanup time for effective completion of phytoextraction programs requires a model of metal uptake by tolerant plants (Maxted et al. 2007).

Several studies have been carried out to model metal phytoextraction (Brennan and Shelley 1999; Chrysafofopoulou et al. 2005; Khodaverdiloo and Homaei 2008; Verma et al. 2007). These models have often been established based on a single metal ion system, while soil contamination by heavy metals is not often limited to a single contaminant. The competition among heavy metals would affect their distribution in different phases of the soil; non-specific and specific sorptions of different metal ions are suppressed by competition to varying extents (Serrano et al. 2005). Although some interesting studies have been carried out dealing with in situ phytoextraction in multi-contaminated soil, (do Nascimento et al. 2006; Hammer and Keller 2003; Papazoglou 2011; Yahu et al. 2013), a very little attention has been focused on modeling phytoextraction in multi-metal conditions (Quartacci et al. 2006; Yip et al. 2009). Therefore, the objectives of this study were (a) to assess the uptake ability and behavior of ornamental kale and land cress plants grown in a calcareous soil contaminated by separate and combined Ni and Cd and (b) to develop a simple practical model to predict the cleanup time for separate and simultaneous remediation of Ni and Cd from contaminated soils.

## Materials and methods

### Model derivation

An analytical model was derived to account for simultaneous phytoextraction of Ni and Cd from contaminated soils. The derivation was performed based on the assumption that both Ni and Cd are simultaneously present within the soil medium. Considering the total mass of Ni ion within different phases of soil as  $M_{T(Ni)}$  ( $M L^{-3}$ ), we have

$$M_{T(Ni)} = \Gamma_{Ni}\rho_b + c_{Ni}\theta + M_{P(Ni)} \quad (1)$$

where  $\Gamma_{Ni}$  ( $M M^{-1}$ ) is the Ni concentration on surface adsorption sites,  $\rho_b$  ( $M L^{-3}$ ) is the soil bulk density,  $c_{Ni}$  ( $M L^{-3}$ ) is the Ni concentration in the soil liquid phase,  $\theta$  ( $L^3 L^{-3}$ ) is the

volumetric water content, and  $M_{P(Ni)}$  ( $M L^{-3}$ ) is the Ni concentration in unit volume of the soil solid (precipitated) phase.

Since, metal ion concentration in equilibrium with the mineral phases (usually metal hydroxides) is quite low and this process is not kinetically favored, it can be assumed that Ni concentration in the soil solid phase ( $M_{P(Ni)}$ ) is not readily available for plants; hence, Eq. (1) can be rewritten for a given volume of bulk soil ( $V$ ) as

$$M_{v(Ni)} = V(\Gamma_{Ni}\rho_b + c_{Ni}\theta) \quad (2)$$

where  $M_{v(Ni)}$  ( $M$ ) is the total mass of Ni per soil volume  $V$  ( $L^3$ ).

The phytoextraction rate can now be considered as the remediated amount of contaminant by plants per unit volume of soil at unit time. Thus,

$$Vr_{o(Ni)} = \frac{dM_{v(Ni)}}{dt_{Ni}} = \frac{d[V(\Gamma_{Ni}\rho_b + c_{Ni}\theta)]}{dt_{Ni}} \quad (3)$$

$$r_{o(Ni)} = \frac{d(\Gamma_{Ni}\rho_b + c_{Ni}\theta)}{dt_{Ni}}$$

where  $r_{o(Ni)}$  ( $M L^{-3} T^{-1}$ ) is the phytoextraction rate of the target contaminant and  $t$  ( $T$ ) is time.

For a binary ion adsorption system, the relationship between the adsorbed and dissolved Ni concentrations can be expressed by a linear adsorption equation:

$$\Gamma_{Ni} = K_{d(Ni)}c_{Ni}c_{Cd} + \delta_{Ni} \quad (4)$$

where  $K_{d(Ni)}$  ( $L^3 M^{-1}$ )<sup>2</sup> is the distribution coefficient of Ni ion,  $c_{Cd}$  ( $M L^{-3}$ ) is Cd concentration in the soil liquid phase, and  $\delta_{Ni}$  is a measure of irreversible adsorbed Ni ( $M M^{-1}$ ).

Substituting Eq. 4 into Eq. 3 gives

$$r_{o(Ni)} = \frac{d((K_{d(Ni)}c_{Ni}c_{Cd} + \delta_{Ni})\rho_b + \theta c_{Ni})}{dt_{Ni}} \quad (5)$$

Rearranging Eq. 5 gives

$$dt_{Ni} = \frac{(K_{d(Ni)}c_{Cd}\rho_b + \theta)dc_{Ni}}{r_{o(Ni)}} \quad (6)$$

In order to characterize the kinetics behavior of this system, it is necessary to determine how the phytoextraction rate ( $r_o$ ) varies with different contaminant concentrations. Three basic assumptions can be considered in this regard as (a)  $r_{o(Ni)}$  does not depend on total soil Ni concentration (Eq. 7), (b)  $r_{o(Ni)}$  proportionally depends on total soil Ni concentration (Eq. 8), and (c)  $r_{o(Ni)}$  inversely depends on total soil Ni concentration (Eq. 9):

$$r_{o(Ni)} = \frac{-dc_{Ni}}{dt_{Ni}} = k_0 \quad (7)$$

$$r_{o(Ni)} = \frac{-dc_{Ni}}{dt_{Ni}} = k_1 c_{Ni} \tag{8}$$

$$r_{o(Ni)} = \frac{-dc_{Ni}}{dt_{Ni}} = \frac{k_2}{c_{Ni}} \tag{9}$$

Substituting  $r_{o(Ni)}$  from these three presumptions into Eq. 6 and integrating over a period of time from 0 to  $t_r$  and for concentration range from  $c_{(Ni)0}$  to  $c_{(Ni)f}$  we get

$$\int_0^{t_r(Ni)} dt_{Ni} = \frac{(K_{d(Ni)}c_{Cd}\rho_b + \theta)}{k_0} \int_{c_{(Ni)0}}^{c_{(Ni)f}} dc_{Ni} \tag{10}$$

$$\int_0^{t_r(Ni)} dt_{Ni} = \frac{(K_{d(Ni)}c_{Cd}\rho_b + \theta)}{k_1} \int_{c_{(Ni)0}}^{c_{(Ni)f}} \frac{dc_{Ni}}{c_{Ni}} \tag{11}$$

$$\int_0^{t_r(Ni)} dt_{Ni} = \frac{(K_{d(Ni)}c_{Cd}\rho_b + \theta)}{k_2} \int_{c_{(Ni)0}}^{c_{(Ni)f}} c_{Ni} dc_{Ni} \tag{12}$$

The required time for phytoextraction of soil Ni ( $t_{r(Ni)}$ ) in a competitive binary ion system can be obtained by integrating Eqs. 10, 11, and 12 as

$$t_{r(Ni)} = \left( \frac{K_{d(Ni)}c_{Cd}\rho_b + \theta}{k_0} \right) (c_{(Ni)0} - c_{(Ni)f}) \tag{13}$$

$$t_{r(Ni)} = \left( \frac{K_{d(Ni)}c_{Cd}\rho_b + \theta}{k_1} \right) \ln \frac{c_{(Ni)0}}{c_{(Ni)f}} \tag{14}$$

$$t_{r(Ni)} = \left( \frac{K_{d(Ni)}c_{Cd}\rho_b + \theta}{2k_2} \right) (c_{(Ni)0}^2 - c_{(Ni)f}^2) \tag{15}$$

where  $k_0$  ( $M L^{-3} T^{-1}$ ),  $k_1$  ( $T^{-1}$ ), and  $k_2$  ( $M^2 L^{-6} T^{-1}$ ) are the coefficients of phytoextraction rate,  $c_{(Ni)0}$  is Ni concentration in the soil solution at the beginning of phytoextraction

process, and  $c_{(Ni)f}$  is the acceptable Ni concentration in soil solution.

Equations 13, 14, and 15 can be also rewritten to predict the cleanup time for phytoextraction of either Ni or Cd in single ion systems.

### Soil characterization

In order to verify the proposed phytoextraction model, an extensive experiment was conducted with ornamental kale and land cress under controlled conditions in a calcareous soil. Soil samples were collected from an uncontaminated agricultural field, air-dried for 7 days, and sieved through a 4.8 mm sieve. Some physical and chemical properties of the experimental soil were measured according to the standard procedures. Particle size distribution and bulk density were measured by the hydrometry and core methods, respectively (Klute 1986). Organic carbon (OC) was determined by the Walkley-Black method. Calcium carbonate equivalent (CCE) was measured by titration method. Soil pH was determined in 1:2.5 soil/solution ratio. Electrical conductivity (EC) was measured in 1:1 soil/solution ratio. Cation exchange capacity (CEC) was determined using the 1 M  $NH_4OAC$  (pH=7) method (Page 1983). The obtained results are presented in Table 1.

### Pot experiments

Different concentrations of Ni (0, 50, 100, 250, 500, and 1000  $mg\ kg^{-1}$ ) and Cd (0, 3, 5, 10, 25, and 50  $mg\ kg^{-1}$ ) were imposed to a large quantity of soil, using  $NiCl_2$  and  $CdCl_2$ , respectively. The soil samples were then thoroughly mixed, homogenized, and subsequently packed into cylindrical lysimeters of 30 cm height and 22 cm diameter (each in three replicates). The soil samples were carefully packed to attain a uniform bulk density of  $1500\ kg\ m^{-3}$  in all experimental lysimeters. Prior to sowing, the lysimeters were maintained at field capacity status for 70 days in order to equilibrate chemically with the applied heavy metals. To prevent leaching of contaminants from the lysimeters, no drainage was allowed. Three ornamental kale (*Brassica oleracea* var. *viridis*) and 15 land cress

**Table 1** Some physical and chemical properties of the experimental soil

Silt (%)	Silt	Sand	Soil texture	$\rho_b$ ( $kg\ m^{-3}$ )	OC (%)	CEC ( $cmol\ kg^{-1}$ )	CCE (%)	pH	EC ( $dS\ m^{-1}$ )
28	29	43	Clay loam	1500	0.18	13.67	13	7.6	0.2

(*Lepidium sativum*) seeds were sown in the experimental lysimeters under controlled environmental conditions. One week later, the seedlings of ornamental kale and land cress were thinned to one and nine plants, respectively. To prevent evaporation from soil surface, the top of each lysimeter was covered by inert granules. The lysimeters were irrigated with tap water throughout the growth period, as such soil water content was maintained in the range of 0.8 FC to FC. The basic nutrient requirements of plants were applied in solution form together with irrigation water to prevent any possible nutrient deficiency. The ornamental kale and land cress were respectively harvested at 180 and 60 days after transplantation in the contaminated soils. Leaf area index (LAI) was determined by the leaf area meter apparatus. For further analysis, plant samples were washed thoroughly with tap water to remove unwanted debris and blotted dried and then rinsed with distilled water. Plant tissues were cut into small pieces, dried for 2 days at 80 °C, and then weighted. Dried plant samples were grounded with stainless steel mill and passed through a 0.25 mm sieve prior to metal analysis. The Ni and Cd in subsamples of plant material were extracted by wet oxidation method (Gupta 2009). Nickel and Cd concentrations were measured by either atomic

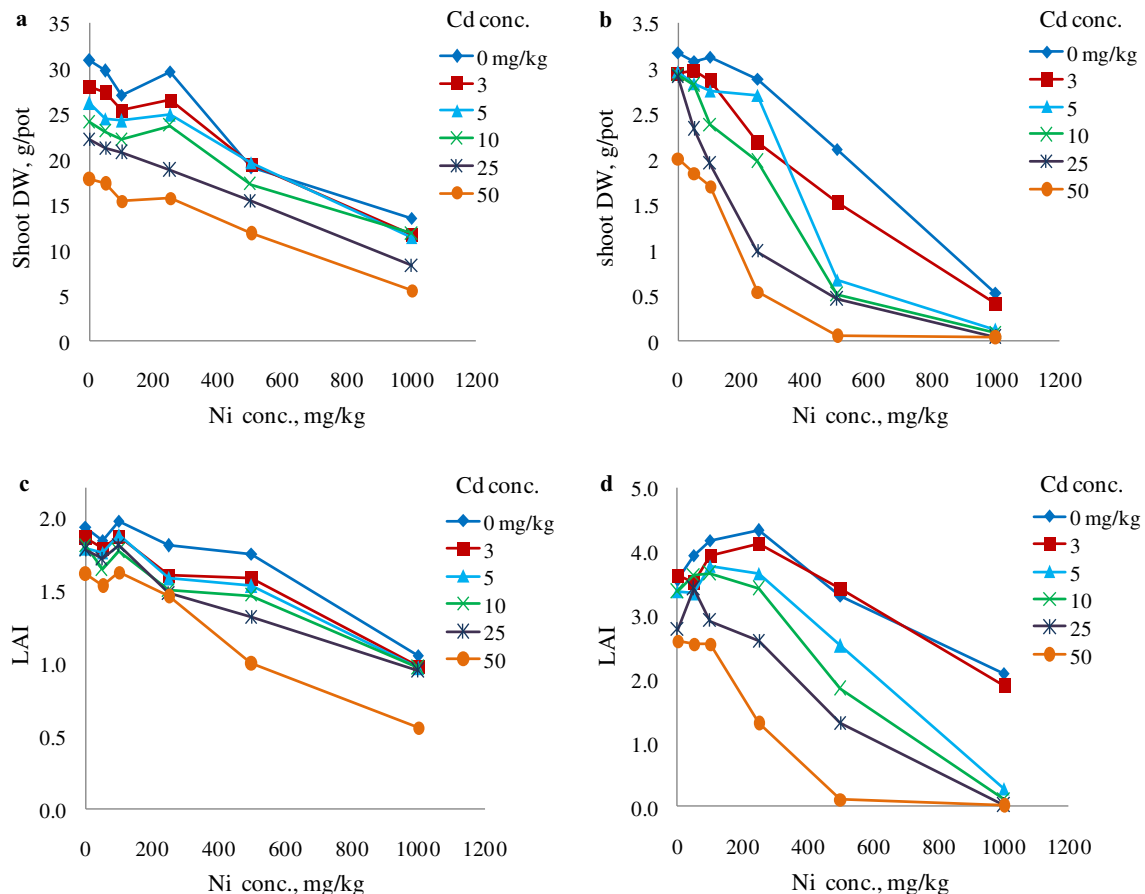
absorption spectrophotometer (Shimadzu, AA 670-G) or inductively coupled plasma optical emission spectrometry (Varian Vista-PRO), depending on metal ion concentration in solutions. After harvesting plants, the soil samples of each lysimeter were air-dried and screened through a 2 mm sieve. The dissolved fraction of Ni and Cd ions were extracted by equilibrating soil samples with distilled water for 24 h in 1:2 soil/solution ratio (Gupta 2009). The metal ion concentration in the extracted solution was directly analyzed by AAS or ICP-OES instruments.

#### Adsorption experiments

The Ni and Cd adsorption and desorption experiments were carried out on the experimental calcareous soil in both single and binary ion systems. The experimental data were described by using the linear adsorption equation.

#### Data analysis

The derived models were fitted on the phytoextraction experimental data using CurveExpert 1.38. The



**Fig. 1** The effect of soil Ni concentrations on shoot dry weight and leaf area index of ornamental kale (a, c) and land cress (b, d) at the presence of Cd

performance of the proposed models was evaluated using the modeling efficiency (EF), normalized root mean square error (NRMSE), and maximum error (ME) statistics (Ghorbani Dashtaki et al. 2009; Homaei et al. 2002):

$$EF = 1 - \frac{\sum_{i=1}^n (P_i - \bar{O})^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \tag{16}$$

$$NRMSE = \left[ \frac{\sum_{i=1}^n (P_i - O_i)^2}{n} \right]^{1/2} \frac{100}{\bar{O}} \tag{17}$$

$$ME = \max |P_i - O_i|_{i=1}^n \tag{18}$$

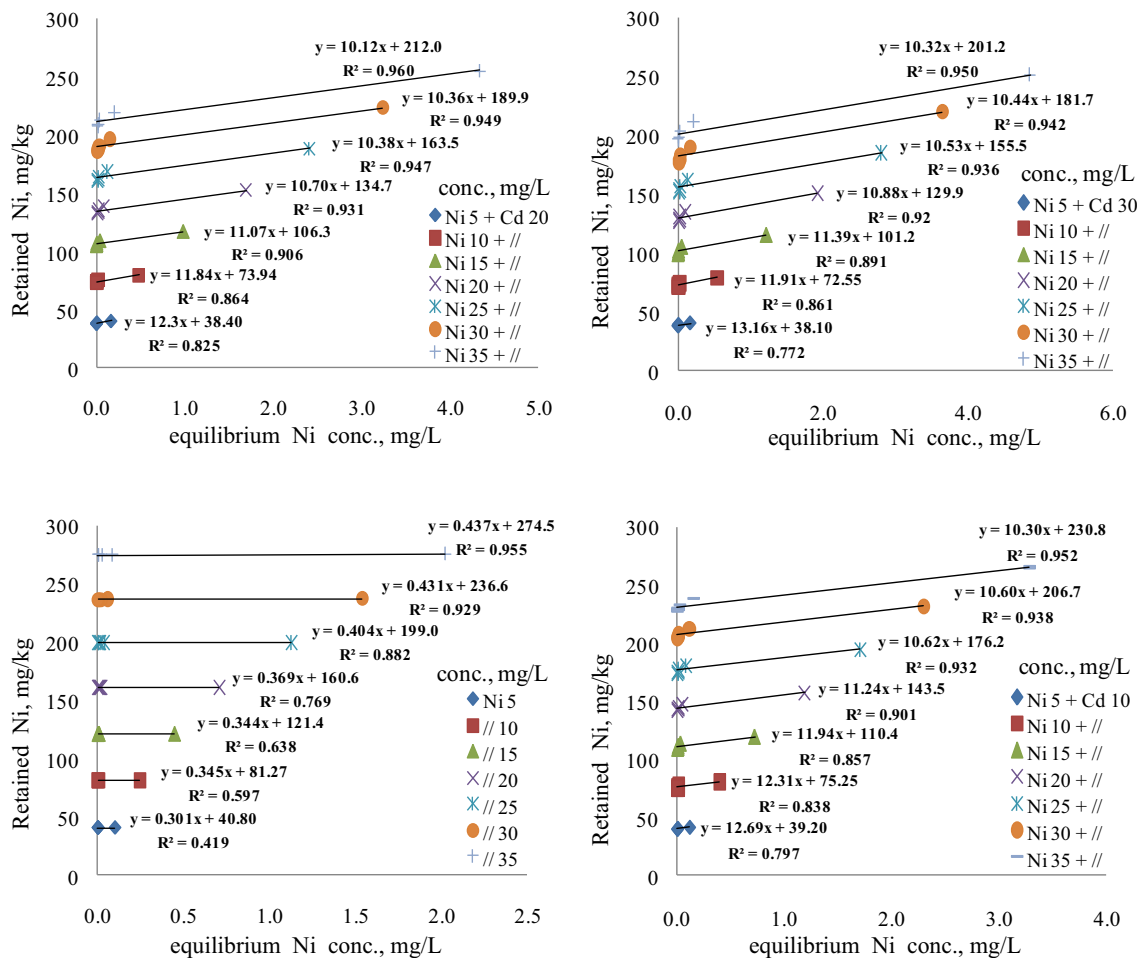
where  $P_i$  is the predicted (simulated) values,  $O_i$  is the observed (measured) values,  $\bar{O}$  is mean of the observations, and  $n$  is the

number of samples. The EF value compares the simulated values to the averaged measured values. The maximum value for EF is 1. The EF value can be negative. A negative EF value indicates that the averaged measured values give a better estimate than the simulated values. The lower limit for NRMSE and ME is 0. The large NRMSE value shows how much the simulations overestimate or underestimate the measurements, while the large ME value represents the worst case performance of the model. If all simulated and measured data are the same, the statistics yield EF=1, NRMSE=0, and ME=0 (Nouri et al. 2014; Zarei et al. 2010).

### Results and discussion

Effect of Ni and Cd contaminations on ornamental kale and land cress growth

Successful phytoremediation depends on produced plant biomass and elemental concentrations within the plants. The effects of separate and combined Ni and Cd contaminants on shoot dry weights of ornamental kale and land cress are



**Fig. 2** Adsorption and desorption isotherms of Ni at the presence of 0, 10, 20, and 30 mg Cd L<sup>-1</sup> and the model description by the linear adsorption equation

presented in Fig. 1. These experimental data indicate that shoot dry weight of both plants has a diminishing trend under various Ni and Cd concentrations. This effect is much more significant for Cd than for Ni. The observed depressing influence of Ni and Cd can be related to their elevated bioavailability. Similar depressing effects at the presence of Ni have been reported for radishes (Simon et al. 2000), fenugreek (Parida et al. 2003), broad bean (Srivastava et al. 2005), wheat (Ouzounidou et al. 2006) and barley, and tomato (Rooney

et al. 2007). Some other reports are also available at the presence of Cd for marigold, chrysanthemum and gladiolus (Lal et al. 2008), *Brassica napus* cocropped with *B. parachinensis* or *Zea mays* (Selvam and Wong 2009), radish (Asadi Kapourchal et al. 2009), wheat (Jafarnejadi et al. 2011), and tobacco (Maaroufi Dguimi et al. 2009). According to Fig. 1a, the declining trend of shoot dry weight of ornamental kale at the presence of various Ni concentrations (0–1000 mg kg<sup>-1</sup> soil) is almost similar to that of Cd (0–50 mg kg<sup>-1</sup> soil).

**Table 2** Cd and Ni concentrations (mg kg<sup>-1</sup>) in shoots and roots of ornamental kale and land cress and bioaccumulation factor (BF)

Treatments			Ornamental kale		BF <sub>shoot</sub>	Land cress		BF <sub>shoot</sub>
			Shoot	Root		Shoot	Root	
Ni	Ctrl		3.4	2.5	–	5.0	19.4	–
	Ni <sub>50</sub>		9.1	10.5	0.18	12.2	103.3	0.24
	Ni <sub>100</sub>		14.6	15.9	0.15	17.3	163.5	0.17
	Ni <sub>250</sub>		19.5	24.0	0.08	23.7	350.8	0.09
	Ni <sub>500</sub>		18.2	25.2	0.04	27.6	456.8	0.06
	Ni <sub>1000</sub>		24.8	56.0	0.02	51.8	480.0	0.05
Cd	Ctrl		2.5	0.0	–	8.4	1.8	–
	Cd <sub>3</sub>		4.4	2.5	1.46	60.2	50	20.08
	Cd <sub>5</sub>		5.3	3.2	1.07	135.4	112.5	27.08
	Cd <sub>10</sub>		9.4	10.0	0.94	182.6	149.8	18.26
	Cd <sub>25</sub>		14.4	13.7	0.57	233.5	194.1	9.34
	Cd <sub>50</sub>		19.3	34.9	0.39	257.5	209.1	5.15
Ni in	Ni <sub>50</sub>	+Cd <sub>3</sub>	8.6	12.8	0.17	12.2	73.7	0.24
	Ni <sub>100</sub>		15.6	16.4	0.16	18.2	123.3	0.18
	Ni <sub>250</sub>		15.3	26.2	0.06	23.5	274.0	0.09
	Ni <sub>500</sub>		25.0	38.2	0.05	28.1	435.1	0.06
	Ni <sub>1000</sub>		26.1	57.8	0.03	33.8	524.0	0.03
	Ni <sub>50</sub>	+Cd <sub>5</sub>	8.4	10.3	0.17	12.8	109.4	0.26
	Ni <sub>100</sub>		14.1	17.5	0.14	15.7	171.1	0.16
	Ni <sub>250</sub>		15.3	29.6	0.06	25.1	212.0	0.06
	Ni <sub>500</sub>		19.3	20.4	0.04	35.2	340.8	0.07
	Ni <sub>1000</sub>		24.8	59.6	0.02	36.7	–	0.04
	Ni <sub>50</sub>	+Cd <sub>10</sub>	9.9	13.2	0.20	12.2	88.3	0.30
	Ni <sub>100</sub>		14.2	17.6	0.14	15.0	184.3	0.15
	Ni <sub>250</sub>		17.1	41.2	0.07	23.2	250.4	0.09
	Ni <sub>500</sub>		21.2	37.4	0.04	37.8	402.0	0.08
	Ni <sub>1000</sub>		25.3	48.4	0.03	36.4	–	0.04
	Ni <sub>50</sub>	+Cd <sub>25</sub>	10.2	11.5	0.20	12.1	83.3	0.24
	Ni <sub>100</sub>		14.9	19.2	0.15	14.4	173.5	0.14
	Ni <sub>250</sub>		17.3	33.3	0.07	22.3	235.6	0.05
	Ni <sub>500</sub>		19.4	29.9	0.04	–	–	0.05
	Ni <sub>1000</sub>		21.5	54.8	0.02	–	–	–
	Ni <sub>50</sub>	+Cd <sub>50</sub>	8.1	16.3	0.16	13.6	105.2	0.29
	Ni <sub>100</sub>		12.2	13.8	0.12	14.6	177.8	0.14
	Ni <sub>250</sub>		17.5	30.1	0.07	25.8	241.5	0.10
	Ni <sub>500</sub>		19.9	28.7	0.04	–	–	–
Ni <sub>1000</sub>		20.0	52.4	0.02	–	–	–	



However, this trend for shoot dry weight of land cress at the presence of soil Ni was quite different from that of Cd (Fig. 1b). In the Cd treatments (0–50 mg kg<sup>-1</sup> soil), land cress demonstrated relatively higher resistance than to the Ni (0–1000 mg kg<sup>-1</sup> soil) contaminations.

The growth and development of both plants were affected stronger in the binary ion than in single ion treatments. The results further indicated that shoot dry weight of both plants was decreased by increasing both Ni and Cd concentrations in soil. The lowest shoot dry weight was obtained at the presence of 50 mg kg<sup>-1</sup> Cd in combination with various Ni concentrations, indicating strong toxicity of Cd ion for plants. The Cd ion toxicity was gradually enhanced by increasing Ni ion concentration, most likely due to the adsorption competition, which increases both Ni and Cd availability for plants. These results were supported by the Ni-Cd adsorption-desorption isotherms in which Ni adsorption was decreased by increasing initial Cd concentration (Fig. 2). The higher shoot dry weight of ornamental kale may indicate that it is more tolerant to both Ni and Cd contaminants than land cress.

The obtained root dry weights showed similar trends as that of shoot dry weights at the presence of Ni and Cd treatments. The metal ions were, however, restricted root growth more than that of shoot growth. This effect was stronger in Ni+Cd treatments than at the presence of either Ni or Cd. This can be attributed to the competitive effect of Ni and Cd ions that hindered the root development (data not shown). Beside the effect of Ni and Cd on plant biomass, LAI of both plants exhibited progressive reduction by increasing Ni and Cd concentrations (Fig. 1c, d). The maximum inhibition was observed in 50 mg Cd kg<sup>-1</sup> soil, combined with various Ni concentrations. The results indicated that LAI of land cress is more affected by Ni and Cd concentrations compared to ornamental kale. These results reveal an antagonistic effect between these two ions on both plants under combined Ni and Cd contaminations. Because, their separate effects on growth parameters were less than that of the combined metals. Thus, the presence of Cd leads to increase toxicity effects of

Ni on plant growth. Similar results have been observed in barley for Cu and Zn (Beckett and Davis 1978), in lettuce, spinach, wheat, endive, and maize for Zn and Cd (Smilde et al. 1992), in cucumbers for Cu, Cd, and Pb (An et al. 2004), and in cardoon for Cd and Ni (Papazoglou 2011). Our observations indicate that the antagonistic effect of Ni and Cd on land cress is more significant than on ornamental kale. These results clearly imply that toxicity of heavy metals varies with plant species.

#### Ni and Cd uptake by ornamental kale and land cress

Since differences in biomass weight can give an apparent increase/decrease in uptake concentrations, the overall metal uptake was also measured. Table 2 reports concentrations of Ni and Cd in the shoots and roots of ornamental kale and land cress grown in the contaminated soils. According to Table 2, the Ni and Cd contents in both plants were increased by increasing their concentrations in soil for all single and binary ion treatments. In the Cd-contaminated treatments, Cd concentrations in shoots and roots of both plants were elevated. These results further indicate that Cd concentration in shoots is more than that in roots and land cress exhibits a stronger capability to endure Cd toxicity. A plant can be specified as a metal accumulator when its bioaccumulation factor (BF; the metal concentration ratio of plant to soil) is larger than 1. Moreover, if concentrations in shoots surpassed the critical level of 1000 mg kg<sup>-1</sup> for Ni and of 100 mg kg<sup>-1</sup> for Cd, the plant could be described as Ni or Cd hyperaccumulator (Chaney et al. 1997; McGrath and Zhao 2003). The presented data in Table 2 indicate that land cress response to Cd has exceeded the critical level of 100 mg kg<sup>-1</sup> and its BF is larger than 1. Thus, it can be considered as a Cd-accumulator plant. Ornamental kale, however, had relatively weak Cd accumulation into its roots and shoots. Although Cd concentration in ornamental kale did not exceeded the critical level for Cd hyperaccumulation, it surpassed the concentration level of

**Table 3** The values of  $k_0$ ,  $k_1$ , and  $k_2$  for remediating Ni at the presence of Cd by ornamental kale and land cress

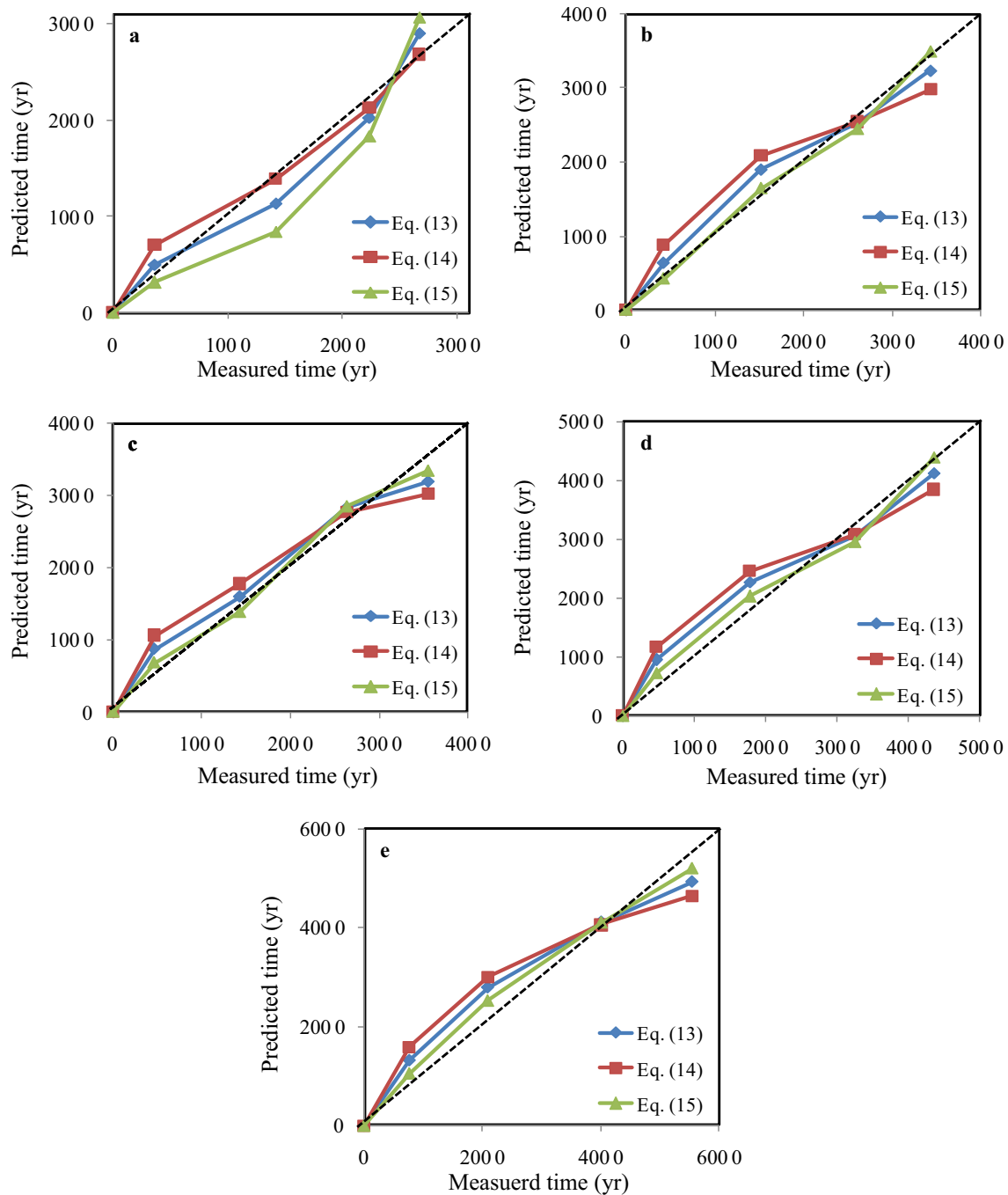
			$k_0$ (mg L <sup>-1</sup> yr <sup>-1</sup> )	$k_1$ (yr <sup>-1</sup> )	$k_2$ (mg <sup>2</sup> L <sup>-2</sup> yr <sup>-1</sup> )
Ornamental kale	Ni+	Cd <sub>3</sub>	$1.87 \times 10^{-5}$	$1.73 \times 10^{-4}$	$4.51 \times 10^{-6}$
		Cd <sub>5</sub>	$1.95 \times 10^{-5}$	$1.71 \times 10^{-4}$	$4.88 \times 10^{-6}$
		Cd <sub>10</sub>	$1.64 \times 10^{-5}$	$1.41 \times 10^{-4}$	$3.99 \times 10^{-6}$
		Cd <sub>25</sub>	$1.84 \times 10^{-5}$	$1.47 \times 10^{-4}$	$4.82 \times 10^{-6}$
		Cd <sub>50</sub>	$1.93 \times 10^{-5}$	$1.45 \times 10^{-4}$	$5.34 \times 10^{-6}$
Land cress	Ni+	Cd <sub>3</sub>	$9.48 \times 10^{-6}$	$9.25 \times 10^{-5}$	$2.24 \times 10^{-6}$
		Cd <sub>5</sub>	$5.06 \times 10^{-6}$	$3.56 \times 10^{-5}$	$1.48 \times 10^{-6}$
		Cd <sub>10</sub>	$4.94 \times 10^{-6}$	$3.97 \times 10^{-5}$	$1.29 \times 10^{-6}$
		Cd <sub>25</sub>	$4.27 \times 10^{-6}$	$3.51 \times 10^{-5}$	$1.04 \times 10^{-6}$
		Cd <sub>50</sub>	$9.85 \times 10^{-6}$	$7.50 \times 10^{-5}$	$2.68 \times 10^{-6}$

0.01–0.2 mg kg<sup>-1</sup> found in most plants (Kabata-Pendias and Mukherjee 2007).

The Ni accumulation within shoots and roots of both plants was also increased by increasing soil Ni concentration. In the 1000 mg Ni kg<sup>-1</sup> soil treatment, they reached up to 24.8, 56.0, 51.8, and 480.0 mg kg<sup>-1</sup>, respectively. The obtained results further showed that land cress has relatively poor capability to take up Ni from soil and translocate it to its aboveground parts. Ornamental kale showed a great capability to take up and

accumulate Ni in its root tissues but failed to translocate it to its shoots. It can be then concluded that ornamental kale should not be considered as a Ni accumulator plant. However, shoot Ni concentration of both plants exceeded the concentrations of 0.1–5 mg kg<sup>-1</sup> found in most plants (Kabata-Pendias and Mukherjee 2007).

In the binary ion treatments, Ni concentration in tissues of both plants was increased by increasing soil Ni concentration in all Cd levels. At constant Ni concentration, increase in Cd



**Fig. 3** The cleanup time for remediating Ni at the presence of **a** 3, **b** 5, **c** 10, **d** 25, and **e** 50 mg Cd kg<sup>-1</sup> contaminated soil predicted with Eqs. 13, 14, and 15 by ornamental kale compared to the measured cleanup time

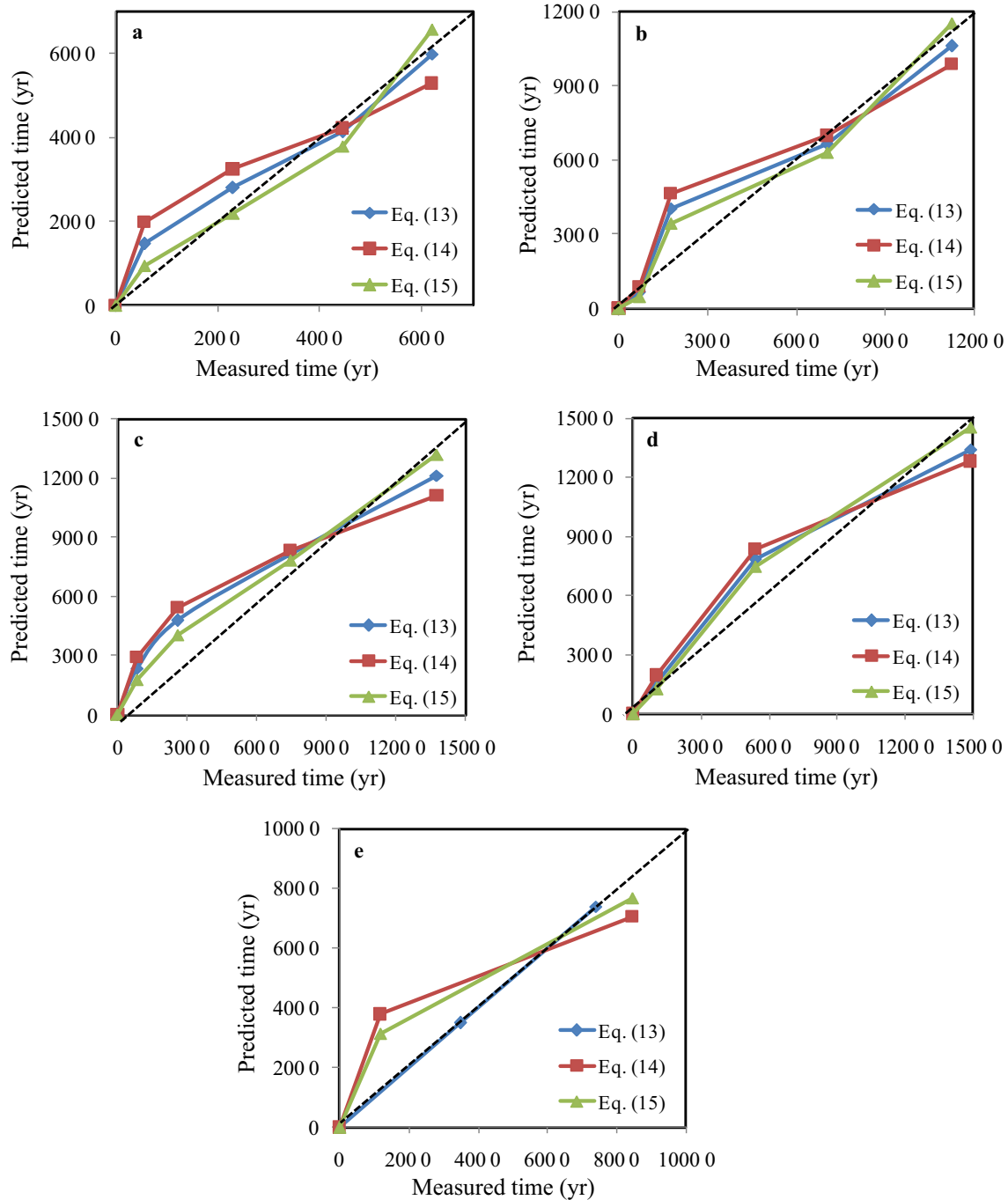


concentration did not appreciably changed the Ni content of both plants. These findings are somewhat in conflict with the competitive adsorption and desorption isotherms of Ni and Cd (Fig. 2), where it was found that an increase in Cd concentration decreases Ni adsorption. Less adsorption favors more plant uptake. This may denote that Ni availability in soil was not a limiting factor in plant uptake. In the Ni and Ni+Cd treatments, Ni concentration in shoots was more than that in roots and the calculated bioaccumulation factors were less

than 1 (Table 2). In general, the results indicate that land cress tends to take up more Ni and Cd than ornamental kale from soil solution.

Modeling cleanup time for phytoextraction of Ni and Cd

Ni desorption experiments were conducted under 0, 10, 20, and 30 mg L<sup>-1</sup> initial Cd concentrations and were described by using the linear adsorption equation (Fig. 2). Figure 2



**Fig. 4** The cleanup time for remediating Ni at the presence of **a** 3, **b** 5, **c** 10, **d** 25, and **e** 50 mg Cd kg<sup>-1</sup> contaminated soil predicted with Eqs. 13, 14, and 15 by land cress compared to the measured cleanup time

**Table 4** The calculated statistics to evaluate the performance of proposed models (Eqs. 13, 14, and 15)

Contaminant	Equation	Ornamental kale			Land cress			
		EF	ME (year)	NRMSE	EF	ME (year)	NRMSE	
Ni+	Cd <sub>3</sub>	13	0.964	285.8	14.7	0.956	897.8	18.2
		14	0.976	339.4	11.9	0.862	1416.3	32.2
		15	0.878	572.4	26.9	0.973	670.6	14.3
	Cd <sub>5</sub>	13	0.972	374.1	1.8	0.938	2300.5	26.1
		14	0.912	558.2	24.1	0.889	2919.7	34.9
		15	0.995	164.9	22.2	0.962	1694.1	20.4
	Cd <sub>10</sub>	13	0.958	407.8	16.7	0.921	2209.7	29.3
		14	0.911	596.8	24.4	0.845	2874.7	41.0
		15	0.984	222.2	10.3	0.973	1482.4	17.2
	Cd <sub>25</sub>	13	0.958	489.5	17.0	0.939	2441.9	24.4
		14	0.908	701.6	25.3	0.898	2983.1	31.5
		15	0.984	296.9	10.7	0.968	2069.1	17.7
	Cd <sub>50</sub>	13	0.943	700.1	19.7	0.846	2308.9	45.6
		14	0.889	912.5	27.5	0.791	2602.2	53.1
		15	0.981	436.0	11.4	0.895	1955.0	37.7

shows that Ni desorption is gradually increased by increasing initial Ni (loading effect) and Cd (competition effect) concentrations. The loading effect appeared to be less effective than the competition effect. According to the desorption isotherms, the average distribution coefficients ( $K_d$ ) of 0.38, 11.39, 10.97, and 11.23 L kg<sup>-1</sup> were obtained for Ni at the presence of 0, 10, 20, and 30 mg Cd L<sup>-1</sup>, respectively. The observed increase of  $K_{d(Ni)}$  at the presence of various Cd concentrations can be interpreted as increased Ni availability for plant uptake. Since there is no significant difference between  $K_{d(Ni)}$  values at the presence of 10, 20, and 30 mg Cd L<sup>-1</sup>, the average value of 11.20 L kg<sup>-1</sup> was used as  $K_{d(Ni)}$  in the proposed phytoextraction model to determine soil response to different levels of Ni+Cd concentrations. The corresponding  $K_d$  value of 0.314 L kg<sup>-1</sup> was also used for Cd. The values for  $\rho_b$  and  $\theta$  in Eqs. 13, 14, and 15 were assigned to be 1500 kg m<sup>-3</sup> and 0.36 kg kg<sup>-1</sup>, respectively. The values of  $k_0$ ,  $k_1$ , and  $k_2$  were optimized by fitting the proposed model to the experimental data, using least square optimization procedure. None of Eqs. 13, 14, and 15 could provide precise predictions in the range of 0–1000 mg Ni kg<sup>-1</sup> soil combined with 0–50 mg Cd kg<sup>-1</sup> soil. This is possibly due to the relatively high uncertainty in the measured data at the presence of high Ni and Cd concentrations. The proposed model appeared to be reasonably well for simulating the required time for remediation of Ni at the presence of Cd. The calculated cleanup time for remediation of 0–500 mg Ni kg<sup>-1</sup> at the presence of Cd from the contaminated soils by ornamental kale and those predicted by Eqs. 13, 14, and 15 are presented in Fig. 3. The values of  $k_0$ ,  $k_1$ , and  $k_2$  for remediating Ni at the presence of Cd by both plants are given in Table 3. Figure 3 shows a good agreement between the measured times and those predicted with Eq. 15

(with an exception for Ni at the presence of 3 mg Cd kg<sup>-1</sup> soil). Figure 4 plots the measured required time for remediation of 0–500 mg Ni kg<sup>-1</sup> at the presence of Cd from the contaminated soils by land cress and those predicted by Eqs. 13, 14, and 15. According to Fig. 4, a reasonable agreement between the measured and those predicted with Eq. 15 is also found for Ni at the presence of 3, 5, 10, and 25 mg Cd kg<sup>-1</sup> soil. At the presence of 50 mg Cd kg<sup>-1</sup>, the predicted cleanup times by Eq. 13 matched the measured data more closely than Eqs. 14 and 15.

The values of calculated statistics for the measured and predicted cleanup time for remediating Ni at the presence of Cd based on Eqs. 13, 14, and 15 are given in Table 4. These results show a reasonable performance of Eq. 15 for predicting cleanup time of Ni at the presence of Cd by land cress. All statistics given in Table 4 indicate significant difference between performances of Eq. 15 with Eqs. 13 and 14. It can be further followed that Eq. 15 provides reasonably well simulations for remediation of Ni at the presence of 5, 10, 25, and 50 mg Cd kg<sup>-1</sup> soil by ornamental kale. At the presence of 3 mg Cd kg<sup>-1</sup> soil, Eq. 13 gives better results compared to Eqs. 14 and 15 for ornamental kale. Although Eq. 13 was efficient in predicting the Ni cleanup time by land cress,

**Table 5** The cleanup time for phytoextracting Ni and Cd to attain the target values

Plant	Ni <sub>100</sub>	Ni <sub>250</sub>	Ni <sub>500</sub>	Ni <sub>1000</sub>	Cd <sub>5</sub>	Cd <sub>10</sub>	Cd <sub>25</sub>	Cd <sub>50</sub>
Ornamental kale (year)	366	1002	3742	8254	41	89	200	395
Land cress (year)	544	1722	5104	20,758	3	6	24	53

Eq. 15 could also provide acceptable predictions. Thus, for simplicity, we propose Eq. 15 for predicting Ni cleanup time at the presence of Cd by both ornamental kale and land cress. Consequently, one can estimate Ni cleanup time at the presence of Cd by ornamental kale or land cress, assuming that Ni phytoextraction rate decreases by increasing Ni and Cd concentrations in soil within the applied range of contaminants (i.e., Ni 0–500 mg kg<sup>-1</sup> and Cd 0–50 mg kg<sup>-1</sup>). The reduced Ni phytoextraction rate can be attributed to decrease of dry shoot weights whereas Ni shoot concentration is increased. Furthermore, our results suggest that the proposed model (Eq. 15) could provide reasonably well predictions for remediating Cd or Ni from contaminated soils by both plants. The predicted cleanup time of Ni and Cd to attain the target values (total metal concentrations of 3 mg Cd kg<sup>-1</sup> and 50 mg Ni kg<sup>-1</sup>) in the 0–15 cm contaminated soil depth is presented in Table 5. These cleanup times for ornamental kale are 41 and 366 years for Cd<sub>5</sub> and Ni<sub>100</sub>, respectively. The cleanup times with land cress for the same concentrations are 3 and 544 years, respectively. As given in Table 5, ornamental kale has less capability for phytoextracting Ni and Cd from the contaminated soils. Ornamental kale could possibly be used in marginally contaminated soils where its growth would not be impaired and the extraction of heavy metals could be maintained at satisfying levels. Presented data in Table 5 also show that phytoextraction of Cd by land cress is more feasible than Ni. This result indicates that phytoextraction by land cress could help to clean up the moderately Cd-contaminated soils. The cleanup time period would be much longer when Ni and Cd are simultaneously present in soil (Figs. 3 and 4).

**Conclusions**

The proposed phytoremediation model with its linear desorption isotherm could reasonably well predict the cleanup time for remediation of Ni, Cd, and Ni at the presence of Cd in the soil. The model assumes that phytoremediation rate inversely depends on total metal ion concentration in the soil. The inverse relationship implies accumulation of metal ion in plant tissues that constrains plant growth and thus metal ion uptake. Experimental data reveals that land cress grown in calcareous soils contaminated by either or both Ni and Cd can accumulate and tolerate soil Cd. It demonstrated great capability to take up and accumulate Ni within its roots but failed to translocate it to its shoots. Thus, land cress grown in soils contaminated with Ni and Cd could be dangerous as a carrier of these metal ions into the food chain. In contrast, ornamental kale could not tolerate and accumulate elevated concentrations of Ni and Cd in calcareous soils. Hence, ornamental kale cannot be considered as Ni or Cd accumulator, and thus, it is not suitable for Ni and Cd phytoextraction purposes. Competitive adsorption

and desorption reactions of Ni and Cd ions are found to enhance Ni and Cd bioavailability; this reaction, however, had no reasonable effect on metal ion accumulation in plant tissues.

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