

# Sorption, desorption, and speciation of Cd, Ni, and Fe by four calcareous soils as affected by pH

Samaneh Tahervand · Mohsen Jalali

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**Abstract** The sorption, desorption, and speciation of cadmium (Cd), nickel (Ni), and iron (Fe) in four calcareous soils were investigated at the pH range of 2–9. The results indicated that sorption of Fe by four soils was higher than 80 % at pH 2, while in the case of Cd and Ni was less than 30 %. The most common sequence of metal sorption at pH 2–9 for four soils was in the order of  $Fe \gg Ni > Cd$ . Cadmium and Ni sorption as a function of pH showed the predictable trend of increasing metal sorption with increase in equilibrium pH, while the Fe sorption trend was different and characterized by three phases. With regard to the order of Cd, Ni, and Fe sorption on soils, Cd and Ni showed high affinity for organic matter (OM), whereas Fe had high tendency for calcium carbonate ( $CaCO_3$ ). Results of metal desorption using 0.01 M NaCl demonstrated that metal sorption on soils containing high amounts of  $CaCO_3$  was less reversible in comparison to soils containing high OM. In general, Cd and Ni desorption curves were characterized by three phases; (1) the greatest desorption at pH 2, (2) the low desorption at pH 3–7, and (3) the least desorption at pH > 7. The MINTEQ speciation solubility program showed that the percentage of free metals declined markedly with increase of pH, while the percentage of carbonate and hydroxyl species increased. Furthermore, MINTEQ predicted that saturation index (SI) of metals increased with increasing pH.

**Keywords** Cd · Ni · Fe · pH · Sorption · Desorption · Speciation

## Introduction

Anthropogenic activities lead to accumulation of heavy metals in soils and thus extensive contamination of surface soils in many countries, which are poisonous for all living organisms (Lamb et al. 2009). The nature of sorption and desorption processes affects metal solubility and bioavailability in soil (Krishnamurti et al. 1999; Jiang et al. 2012). Three mechanisms: (1) inner-sphere-complexation, (2) outer-sphere-complexation, and (3) diffuse ion swarm may be responsible for ion sorption (Sposito and Schindler 1986; Bradl 2004; Tack 2010; Marchi et al. 2006). The most important factor which affects sorption and desorption of heavy metals in soil is pH (Elliot et al. 1986).

Cadmium (Cd) is a nonessential element (Wagner 1993; Yang et al. 2009), but nickel (Ni) is an essential element for plants that are naturally present in soils. Cadmium and Ni contamination of soils is an important subject as a consequence of anthropogenic activities. Human activities such as atmospheric deposition, phosphate fertilizers, and sewage sludge disposal are the main sources of soil Cd and Ni contamination (Smolders and Mertens 2013). It has been reported that iron (Fe) is one of the important metals in soils and aquatic environments (Sunda and Huntsman 1997; Maldonado and Price 2001; González et al. 2014).

Several previous studies have taken into account one or more factors affecting Cd sorption and desorption which

S. Tahervand (✉) · M. Jalali  
Department of Soil Science, College of Agriculture, Bu-Ali Sina University, Hamedan, Iran  
e-mail: s.tahervand@yahoo.com

include pH, the content of soil organic matter (OM), clay, oxides of Fe and Mn, calcium carbonate ( $\text{CaCO}_3$ ), and temperature (Tipping et al. 2003; Wang et al. 2004; Li et al. 2011; Jalali and Moradi 2013). Bolton and Evans (1996) studied the retention of Cd by soils with a wide range of characteristics. These authors expressed that with increasing pH and Cd concentration, the sorption of Cd was increased in all soils.

Schulthess and Huang (1990) found that the sorption of metals by clays was dependent significantly on solution pH and clay mineral characteristics such as silicon and aluminum oxide surfaces. Soil pH is the main factor affecting on Ni solubility, mobility, and sorption, while clay content, Fe and Mn oxides, and soil OM being in the secondary of significance (Anderson and Christensen 1988; Ge et al. 2000; Suavé et al. 2000; Tye et al. 2004; Iyaka 2011).

Iron mainly is found as ferric-hydroxide under aerobic state in neutral and alkaline soils, so it is insoluble and consequently low phytoavailable in these soils (Vert et al. 2002). In well-aerated calcareous or saline soils, high pH and oxidation condition produce Fe deficiency (Schulin et al. 2010). Jalali and Hemati (2013) indicated that pH, OM, and  $\text{CaCO}_3$  were the main factor affecting Fe availability in paddy soils.

Due to the fact that the goal of this study was to verify the influence of pH on metal sorption, thus, taking into account the hydrolysis constant (pK) is important because the proportion of hydrolyzed species will change with changing soil pH. In other words, proportion of free ions decreases with increasing pH and eventually hydrolyzed species emerge and gradually increase. Metals which have lower pK will be sorbed strongly.

In addition to heavy metal sorption and desorption, the speciation and saturation index (SI) are severely affected by pH. Knowledge of metal speciation and the complex interactions between metals and sorbent surfaces is required for realization of the fate and

transport of metals in soil (Yang et al. 2006). For instance due to the adsorption and precipitation of metals by carbonate in calcareous soils, carbonate has an important role in immobilization of metals (Moral et al. 2005).

So far, many studies have been investigated the influence of soil solution pH on sorption, desorption, and speciation of metals, but little research has been done about (1) Fe sorption and desorption in the wide pH range (previous studies have evaluated them at acidic pHs) and (2) the effect of  $\text{CaCO}_3$  and OM on sorption and desorption of Cd, Ni, and Fe as a function of pH by calcareous soils. Thus, the purpose of this study was to evaluate the influence of pH on sorption, desorption, speciation, and SI of Cd, Ni, and Fe by four calcareous soils with different properties.

## Material and methods

### Soil samples

The surface horizons (0–30 cm) of four calcareous soils varying in their properties from Hamedan Province, Iran, were sampled, air-dried, ground, and passed through a 2-mm sieve prior to being used in this study. Soil pH and electrical conductivity (EC) were determined in deionized water with a soil solution ratio of 1:5 (Rowell 1994). Organic matter content, cation exchange capacity (CEC), and calcium carbonate equivalent (CCE) were determined by the dichromate oxidation, neutral 1.0 M  $\text{NH}_4\text{OAc}$  saturation, and acid neutralization procedures, respectively (Rowell 1994). Percentages of sand, silt, and clay were determined by the hydrometer method (Bouyoucos 1962). Total Cd, Ni, and Fe concentrations were measured using 4 M  $\text{HNO}_3$  for 12 h (Sposito et al. 1982). These physicochemical properties of the soils were presented in Table 1.

**Table 1** Physical and chemical properties of studied soils

Soil no.	$\text{CaCO}_3$ %	OM %	pH ( $\text{H}_2\text{O}$ )	EC $\text{dS m}^{-1}$	CEC $\text{cmol}_c \text{ kg}^{-1}$	Sand %	Silt %	Clay %	Texture	Total Cd $\text{mg kg}^{-1}$	Total Ni $\text{mg kg}^{-1}$	Total Fe $\text{mg kg}^{-1}$
1	7.8	1.3	8.3	0.83	5.5	67.5	22.5	10.0	Sandy loam	0.9	34.5	6663.0
2	9.9	4.3	7.3	0.13	21.4	31.5	46.0	22.5	Loam	1.1	98.8	9108.0
3	11.2	2.1	7.7	0.13	22.6	23.5	48.0	28.5	Clay loam	1.5	106.1	9484.5
4	21.5	1.7	8.0	0.18	28.1	19.5	48.0	32.5	Silty clay loam	1.5	123.1	8371.5

$\text{CaCO}_3$  calcium carbonate, OM organic matter, EC electrical conductivity, CEC cation exchange capacity

### Sorption of Cd, Ni, and Fe as a function of pH

One gram of air-dried soil was weighed in duplicate into 50-ml polyethylene centrifuge tubes with 20 ml of 0.6 mM of metal solution (Cd or Ni or Fe) (Merdy et al. 2009) prepared in electrolyte background concentration of 0.01 M NaCl. Suspension pH values were adjusted to 2–9 (Merdy et al. 2009) with increments of 0.5 and 0.7 M HCl or 0.05 M NaOH. The suspensions were shaken for 24 h, and their pH was measured again. A preliminary study of the metal sorption indicated that the suspensions have to be stirred for 24 h after addition of an acid or base to ensure a steady state. Samples were centrifuged at 4000 rpm for 15 min, and supernatant was filtered. Cadmium, Ni, and Fe concentrations in the supernatant were measured by atomic absorption spectrophotometry. Amounts of sorbed Cd, Ni, and Fe were calculated by the difference between the applied and final concentrations in the equilibrium solution.

### Desorption of Cd, Ni, and Fe as a function of pH

In order to perform the desorption experiment, the soil separated from the supernatant solution was washed by distilled water to remove the residual metal in the remaining solution (Harter 1983). Desorption of Cd, Ni, and Fe from the soils was determined using 20 ml of 0.01 M NaCl on remained soil samples from the sorption experiments (Najafi and Jalali 2015). The soil in the tubes was then mixed using a vortex mixer and was

shaken for 24 h. The equilibrated suspensions were centrifuged and filtered as previously described in the sorption experiment. Total metal concentrations in solutions were determined by atomic absorption spectrophotometry. Metals desorbed as a percentage of that sorbed was calculated for different pHs.

### Speciation and saturation index

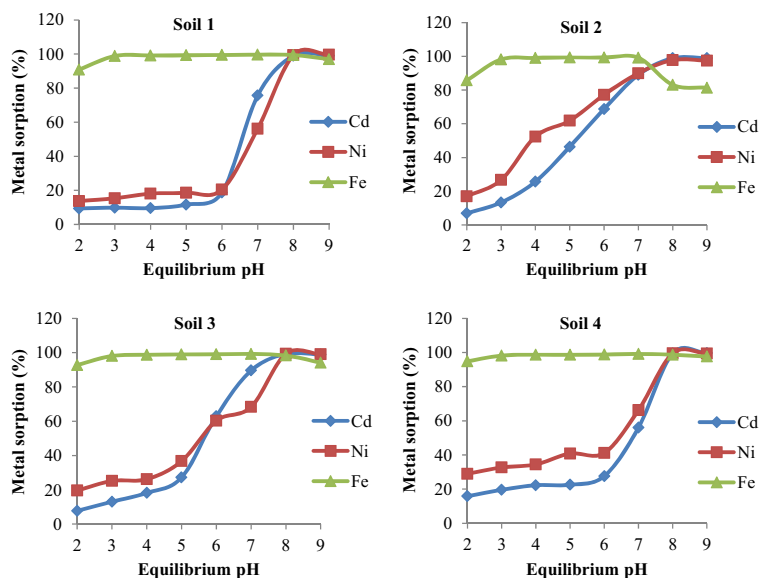
In order to estimate the speciation and SI of Cd, Ni, and Fe in the solution phase, the computer program Visual MINTEQ version 2.30 (Allison et al. 1991) was used. In addition of Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Fe<sup>3+</sup>, concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> in the equilibrium solutions were measured according to the standard methods (Rowell 1994) and used as input to the program for calculating SI and speciation (Jalali and Moradi 2013; Jalali and Hemati Matin 2015).

## Results and discussion

### Sorption experiments

In this study, the sorption of metals was dependent significantly on equilibrium pH (Fig. 1). Increasing solution pH leads to increase the negative surface charge on soil as well as decrease the competition of metal cations with H<sup>+</sup> for sorption sites (Mahdavi et al. 2013), resulting in a more appropriate sorption of metal

**Fig. 1** Sorption of metals as a function of equilibrium pH in different soils



cations by soils (Garcia-Miragaya and Page 1978; Afkhami et al. 2010). Sorption of Cd and Ni showed the predictable trend of increased metal sorption with increasing equilibrium pH (the minimum and maximum sorption of them occurred at pH 2 and 8, respectively in all soils). Many authors suggested that with increasing pH, the retention of the metal cations on soil surfaces increases due to the different mechanisms (Sposito 1989; McBride 1994; Sparks 2003; Appel and Ma 2002; Usman 2008).

The narrow pH range (a transition range) in which rapid increases of sorption occur is called the sorption edge (Loganathan et al. 2012). Comparing the sorption of metals indicated that Cd and Ni initially had a gentle slope in soils 1, 3, and 4, and their sorption edge usually occurred around pHs 5–8 or 6–8, whereas for soil 2, it occurred in the lower pH range (Fig. 1). This would suggest that sorption edge decreases as the OM increases. The result agrees with the observations by Bolton and Evans (1996) that proved that most of the sorption at low pH values occurs on organic surfaces. Also, results of sorption edge and sorption isotherm study of Lee et al. (1996) indicated that different soils had very different sorption capacities for Cd. According to the average metal sorption at all equilibrium pHs, the order of Cd and Ni affinity for soils was soil 2 > soil 3 > soil 4 > soil 1. This sequence demonstrates that the presence of OM generally causes an increase in with these metals sorption. Some studies reported that the presence of high OM in soils mostly results in decrease of Cd and Ni extractability and increase of Zn extractability (McGrath et al. 1988; Arnesen and Singh 1998; Karaca 2004).

The sorption edge for Fe (pH 2–3) was lower than that for Cd and Ni in four soils. Furthermore, Fe sorption trend was different and characterized by three phases (Fig. 1); the fast increasing rate at pH 2–3, followed by a slower or steady rate up to pH 7 (only a slight difference was shown in the sorption of Fe at this pH range) and decreasing phase at pH > 7. The main reason of downward trend at pH > 7 presumably was the presence of Fe as  $\text{Fe}(\text{OH})_4^-$  particularly at pH 9; hence, this negative charge prevented Fe sorption. A notable feature of Fe sorption trend was the greatest decreasing slope in soil 2 (with 4.3 % OM) and then soil 3 (with 2.1 % OM), confirming that the OM enhances the solubility of Fe at high pH. According to Fig. 1, the minimum sorption of this metal in soil 2 occurred at pH > 7. Soil solution pH has a significant effect on Fe solution concentration (Lindsay 1972), and also, there is a significant correlation between the percentage of organic Fe complexes and soil pH (Ammari and Mengel 2006).

Mashhady and Rowell (1978) demonstrated that increasing soil pH from 7.2–9.1 by adding  $\text{Na}_2\text{CO}_3$ , led to increase of Fe solution concentration due to dispersed OM. Also, Gerke (1997) reported that increasing soil pH caused an increase in complexation of Fe by dissolved organic matter (DOM). The least increasing and decreasing slopes (the relatively steady trend) of Fe sorption trend were observed in soil 4 (with 21.5 %  $\text{CaCO}_3$  and 1.7 % OM). This could be related to Fe precipitation. As  $\text{CaCO}_3$  content increases, Fe is precipitated as Fe carbonates and hydroxides (Seatz and Peterson 1964; Rattan and Deb 1981). Selectivity sequence of Fe sorption in the four soils was soil 4 > soil 1 > soil 3 > soil 2, which agrees with the observations by Seatz and Peterson (1964).

We determined  $\text{pH}_{50}$  values for sake of comparing the sorption behavior of metals. The  $\text{pH}_{50}$  value is the pH at which 50 % of sorption occurred (Kinneburgh et al. 1976). Sparks (2003) and Violante et al. (2008) explained that strong sorption of the soil for metals may be considered significant when 50 % of the sorption of metals occurs at lower pH. Furthermore, they reported that the  $\text{pH}_{50}$  position of the sorption edge of metals is affected by hydrolysis or acid–base properties. Figure 1 shows that the  $\text{pH}_{50}$  values for Cd are 5.1 (soil 2), 5.6 (soil 3), 6.6 (soil 1), and 6.8 (soil 4), while for Ni are 3.8 (soil 2), 5.5 (soil 3), 6.4 (soil 4), and 6.8 (soil 1). The average of  $\text{pH}_{50}$  values for Cd and Ni were 6.0 and 5.6, respectively. So Ni had a lower  $\text{pH}_{50}$  value than Cd, which is accordance with Tiller et al. (1984) results. Since the sorption percent of Fe at all equilibrium pHs was higher than 80 %, we could not apply  $\text{pH}_{50}$  value for this metal (Fig. 1).

The most common sequence of metal sorption at pH 2–9 for four soils was in the order of  $\text{Fe} \gg \text{Ni} > \text{Cd}$ . In general, the sorption of Fe at pH 2 was higher than 80 % in four soils, while in the case of Cd and Ni was less than 30 %. High tendency of Fe for sorption is because of the fact that this metal is trivalent. On the other hand, this sequence is not in accordance with sequences of hydrated radius (or ionic radius), atomic weight, electronegativity, and Misono softness value, but it is correlated with  $\text{pK}_1$ . Based on the  $\text{pK}_1$  of Ni which is 9.9 as against the  $\text{pK}_1$  of Cd which is 10.1 (Baes and Mesmer 1976), the sorption of Ni was greater than Cd, as was showed by Antoniadis and Tsadilas (2007).

#### Speciation and saturation indices of Cd, Ni, and Fe

According to the results of MINTEQ speciation solubility program, Cd speciation was significantly affected by

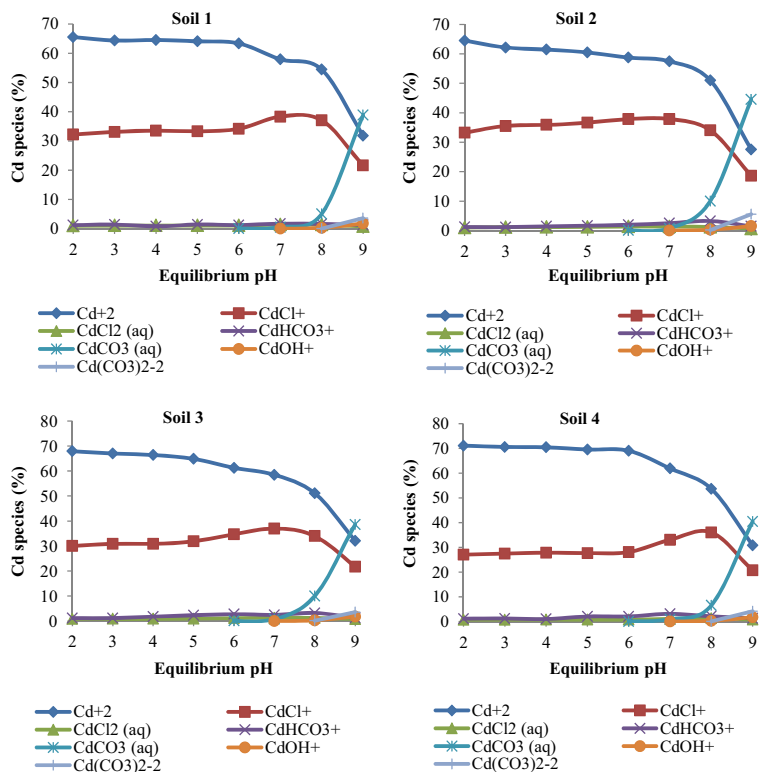
pH (Fig. 2). This program predicted that Cd species such as free Cd (30.6–67.3 %) (average of four soils),  $\text{CdCl}^+$  (20.7–36.5 %),  $\text{CdHCO}_3^+$  (1.2–2.6 %), and  $\text{CdCl}_2$  (aq) (0.8–1.3 %) were observed at all equilibrium pHs. The species of  $\text{CdCO}_3$  (aq) (0.1–40.6 %) and  $\text{Cd}(\text{CO}_3)_2^{2-}$  (0.0–4.2 %) were present at  $\text{pH} \geq 7$ , while  $\text{CdOH}^+$  (0.3–1.7 %) was present at  $\text{pH} \geq 8$  (Fig. 2). Naidu et al. (1994, 1997) found that Cd-hydrolyzed species were present at  $\text{pH} > 8$ , while the predominant species at the pH range of the sorption edge was free Cd. The sorption of metal hydroxyl species to surfaces is preferential than the higher valent-free metal ions (Loganathan et al. 2012). With regard to the percentages listed for Cd species,  $\text{CdCl}^+$  after free Cd had higher percentage. As our result, a number of authors reported that Cd in soils containing high  $\text{Cl}^-$  is more soluble, causing formation of  $\text{CdCl}^+$  complex (McLaughlin et al. 1994; Li et al. 1995; Norvell et al. 2000).

At all equilibrium pHs, Ni predominantly was present as free Ni (40.0–93.8 %) (average of four soils),  $\text{NiHCO}_3^+$  (3.9–16.7 %), and  $\text{NiCl}^+$  (0.1–0.2 %), while  $\text{NiCO}_3$  (aq) (0.1–49.6 %) and  $\text{NiOH}^+$  (0.1–3.6 %) were present at  $\text{pH} \geq 6$  and  $\text{pH} \geq 7$ , respectively (Fig. 3). These are in line with that found by Merrikhpour and Jalali (2013) and

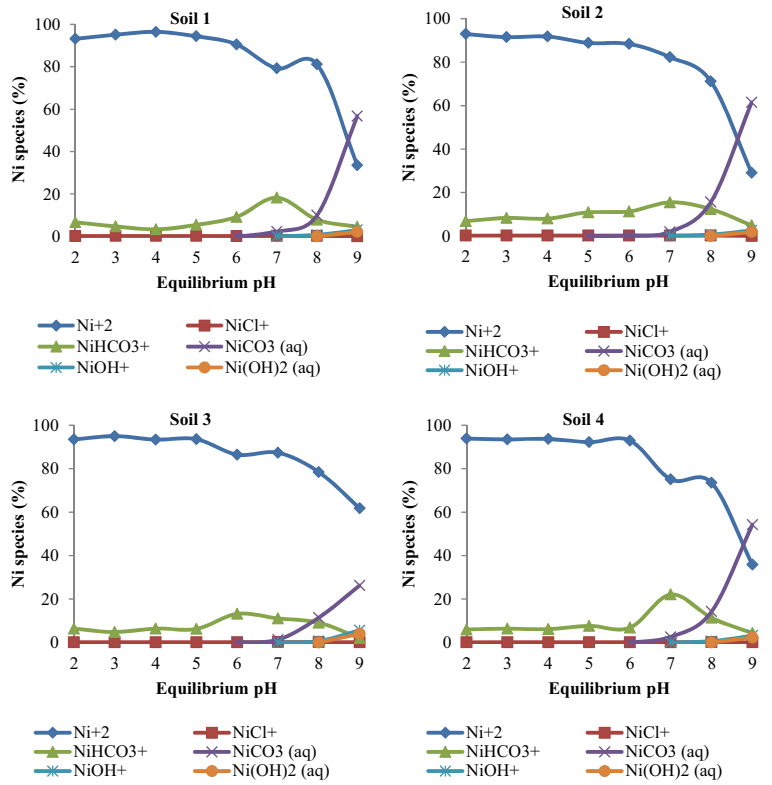
Jalali and Moradi (2013) for Cd and Ni. They observed that in the pH above 7, free Cd and Ni were the major species in soil solution. As Cd, the percentage of free Ni declined markedly with increase of pH, while the percentage of carbonate and hydroxyl species increased (Fig. 3). Precipitation of metals may control their bound to the soil at the high pH values as the sorption is changed to precipitation; hence, metals are precipitated as carbonato-complexes and hydroxy-complexes (Christensen et al. 1996). Ge et al. (2000) observed that  $\text{NiCO}_3$  was the dominant species for Ni in the soil solutions at  $\text{pH} > 8.1$ . The apparent difference of Ni and Fe species with Cd species was the low affinity to form complex with Cl ion at all pHs. Christensen et al. (1996) reported that Cd–Cl complexes may exist at all pH values, while Ni–Cl complexes are imperceptible.

Figure 4 shows that free Fe (0.0–68.2 %) (average of four soils) is present just at pH 2–5 with a decreasing trend. The species of  $\text{FeOH}^{2+}$  (0.1–70.9 %) increased at pH 2–3 while decreased at pH 3–7, indicating that the Fe hydroxides were precipitated even at low pH values. At pH 2–7,  $\text{Fe}(\text{OH})_2^+$  (0.2–99.3 %) increased and then followed by a decreasing trend at pH 7–9. The percent of  $\text{FeCl}^{2+}$  (0.1–7.1 %) decreased at pH 2–4 and was not

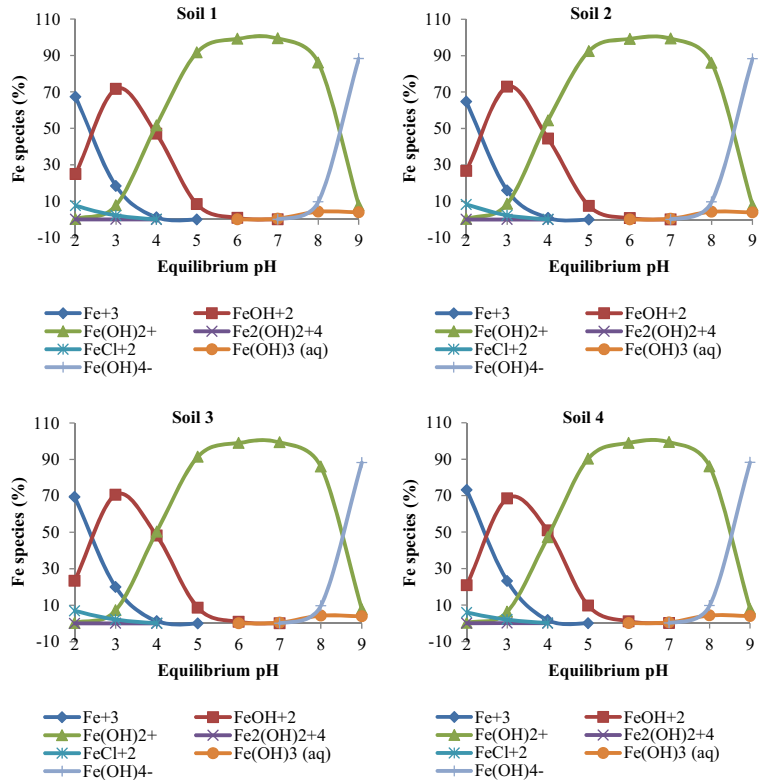
**Fig. 2** Cadmium species as a function of equilibrium pH in different soils



**Fig. 3** Nickel species as a function of equilibrium pH in different soils



**Fig. 4** Iron species as a function of equilibrium pH in different soils



observed at higher pH range. The species of  $\text{Fe}(\text{OH})_3$  (aq) (0.0–4.3 %) was present with an increasingly trend at  $\text{pH} \geq 6$ . At  $\text{pH} \geq 7$ ,  $\text{Fe}(\text{OH})_4^-$  (0.1–88.2 %) had increasingly trend and was not observed at  $\text{pH} < 7$  (Fig. 4). As reports by Lindsay (1979), our calculations showed that the three most abundant species in the pH range of 7–9 were  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_4^-$ .

As can be seen from Figs. 5, 6, and 7, SI of metals increased with increasing pH. In this respect, minimum and maximum SI were observed at pHs 2 and 9, respectively. The MINTEQ program demonstrated that Cd solutions were saturated with respect to otavite at  $\text{pH} \geq 5$  in all soils (Fig. 5). Otavite is a carbonate mineral with  $\text{CdCO}_3$  formula. So we can conclude that  $\text{CO}_3^{2-}$  anion was responsible for Cd precipitation. It was indicated that in calcareous soils, Cd was precipitated as  $\text{CdCO}_3$  (Cavallaro and McBride 1978). Cadmium solutions were undersaturated with respect to  $\text{Cd}(\text{OH})_2$  (s),  $\text{CdCl}_2$  (s),  $\text{CdCl}_2 \cdot 1\text{H}_2\text{O}$  (s),  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (s), and  $\text{CdOHCl}$  (s) (Fig. 5).

For all soils, Ni solutions were saturated with respect to  $\text{NiCO}_3$  (s) and  $\text{Ni}(\text{OH})_2$  (c) at  $\text{pH} \geq 6$  and  $\text{pH} 9$ , respectively, while were undersaturated with respect to  $\text{Ni}(\text{OH})_2$  (am) at all equilibrium pHs (Fig. 6).

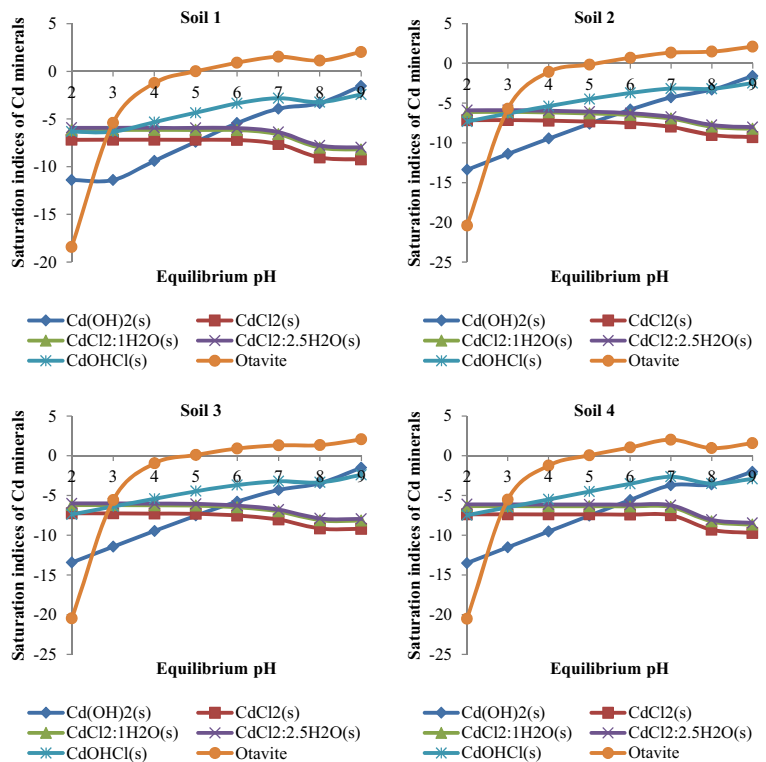
Unlike Ni and Cd, the MINTEQ program predicted no Fe mineral was undersaturated at  $\text{pH} > 4$  in all soils

(Fig. 7). Iron solutions were saturated with respect to hematite, goethite, and  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$  (s) at all equilibrium pHs (the SI of them increased with increasing pH). Furthermore, solutions were saturated with respect to lepidocrocite (at  $\text{pH} > 2$ ), ferrihydrite, ferrihydrite (aged) and maghemite (at  $\text{pH} > 3$ ), and magnesioferrite (at  $\text{pH} > 4$ ) (Fig. 7). This is not in line with that found by Moharami and Jalali (2013) who studied the sorption and desorption of Fe in contaminated calcareous soils in the presence of different cations and anions. They indicated that Fe solubility was controlled by siderite and vivianite at low and high added concentrations of Fe.

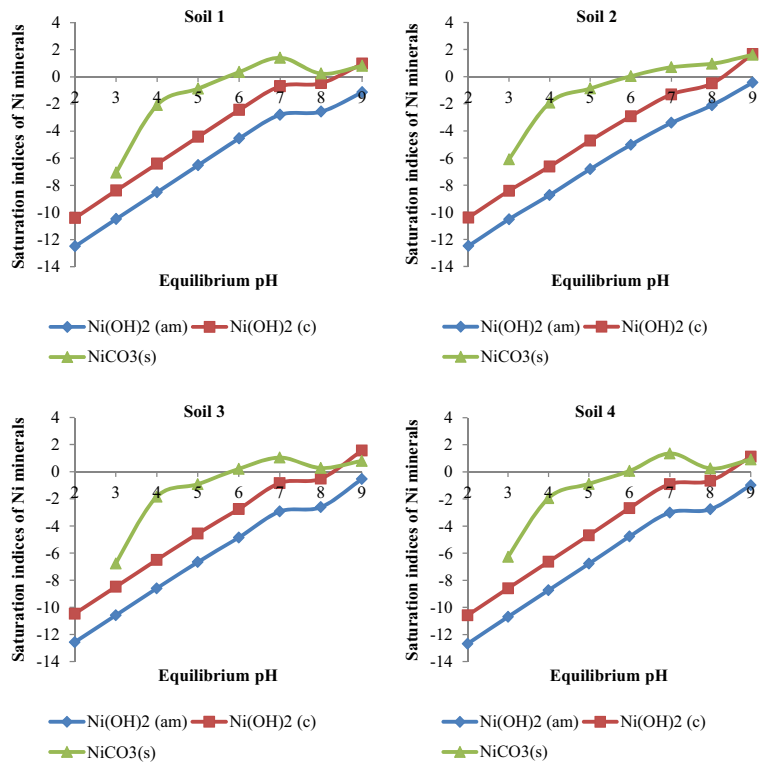
Desorption experiments

Desorption of metals was done by using 0.01 M NaCl as a function of initial pH (equilibrium pH of sorption experiment). The amount of metals desorbed from soils was strongly affected by pH (Fig. 8). Generally, Cd and Ni desorption decreased with increasing initial pH, as was observed by Gray et al. (1998) and Mellis et al. (2004). McBride (1989) indicated that at low pH, some of the adsorbed metals can be displaced by  $\text{H}^+$  ions. Furthermore, Serrano et al. (2009) indicated that in natural soils, Cd sorption at low and high pHs occurs

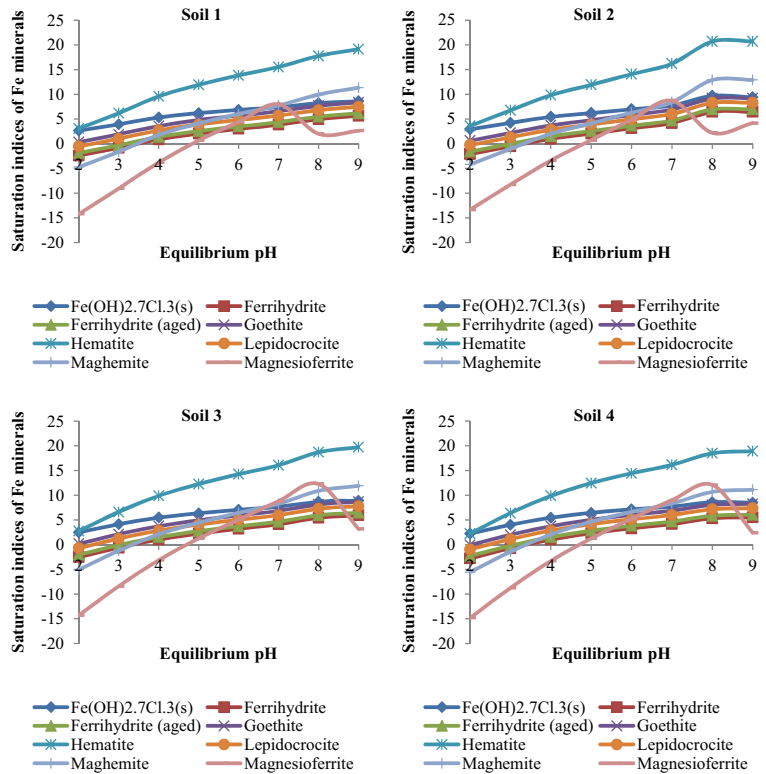
Fig. 5 Saturation indices of Cd minerals as a function of equilibrium pH in different soils



**Fig. 6** Saturation indices of Ni minerals as a function of equilibrium pH in different soils



**Fig. 7** Saturation indices of Fe minerals as a function of equilibrium pH in different soils





via ion exchange and specific sorption, respectively. Thus, as stated above, Cd desorption at low pHs was greater than higher pH values. In general, Cd and Ni desorption curves were characterized by three phases: (1) the greatest desorption at pH 2, (2) the low desorption at pH 3–7, and (3) the least desorption at pH > 7. In contrast to the Cd and Ni, desorption of Fe as a function of pH has an irregular trend (a valley-like curve) and in general, when the pH increased an upward trend was observed except for soil 3 (Fig. 8). Some studies have reported this type of curve for desorption of lead (Pb), copper (Cu), and Cd as affected by organic acids (Gao et al. 2003; Yang et al. 2006; Najafi and Jalali 2015).

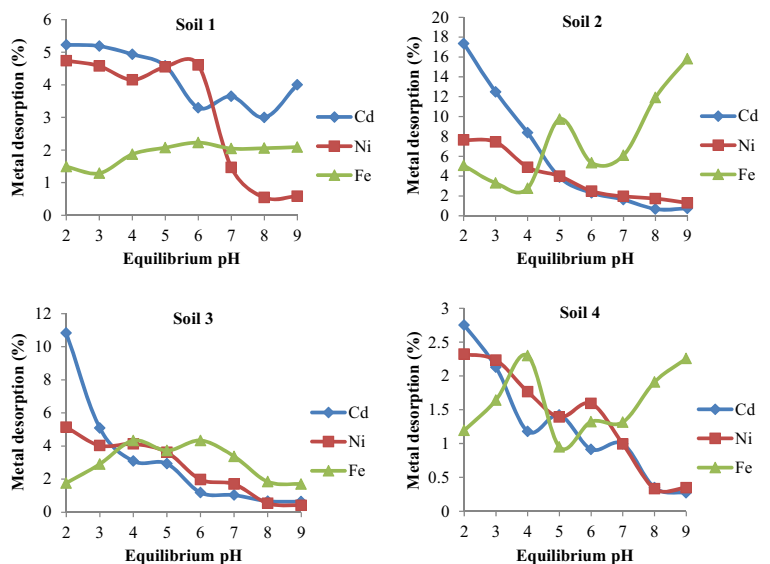
The average desorption values of Cd, Ni, and Fe by four soils at pH 2–9 were 1.2 to 5.9, 1.4 to 3.9, and 1.6 to 7.5 %, respectively. Maximum desorption of Cd and Ni occurred at pH 2 and in soil 2, whereas minimum desorption of them occurred at pH 8–9 and in soil 4 (Fig. 8). So, Cd and Ni sorption in soils containing high amounts of CaCO<sub>3</sub> was less reversible in comparison to soils containing high OM, despite the higher sorption capacity of these soils. It has been reported that the sorption of metals by carbonate is irreversible (Morse 1986). The comparison of the Cd and Ni desorption shown in Fig. 8 shows that Cd desorption is lower than Ni at higher pH values in three soils (except in soil 1 due to the low CaCO<sub>3</sub> content), indicating that calcite has a high tendency for Cd sorption (McBride 1980; Shaheen et al. 2013). Zachara et al. (1991) explained that the hydration energy of Cd is less than Ni, so the sorbed Cd and Ni on calcite form surface precipitate and

surface complex, respectively. In general, Ni sorption was more irreversible than Cd at low pH values. Uren (1992) found that Ni is sorbed preferentially on OM than inorganic surfaces. Moreover, Stevenson (1982) reported that at pH lower than 6.0, less Cd organic complex is formed. For Fe, maximum desorption was observed at pH 9 and in soil 2 (Fig. 8). As stated previously, high pH increases the solubility of OM (Han and Singer 2007) and thus, metal sorption on soil surfaces decreases when metal–DOM complexes increase. This was proved for Pb in a study by Suavé et al. (1998) and for mercury (Hg) in a study by Yin et al. (1996). Minimum desorption of Fe occurred at lower pH ranges and in soil 4 (Fig. 8), confirming that irreversibility of Fe sorption in soil containing high CaCO<sub>3</sub> is greater than other soils, as was observed for Cd and Ni.

### Conclusions

According to the results of present experiments, the following conclusion can be achieved: (1) sorption of metals was greatly dependent on pH with a similar sorption behavior of Cd and Ni and dissimilar sorption behavior of Fe. (2) Sorption and desorption selectivity of soils for metals were dependent on pH, CaCO<sub>3</sub> and OM content, and nature of metals. (3) Sorption experiments demonstrated that Cd and Ni sorption on soil having high OM content was higher than that on other soils, while Fe sorption on soil having high CaCO<sub>3</sub> was

**Fig. 8** Desorption of metals as a function of initial pH (equilibrium pH of sorption experiment) in different soils



higher than soils with high OM. (4) In general, the selectivity sequence of metals sorption in the four soils was  $\text{Fe} \gg \text{Ni} > \text{Cd}$ . (5) Desorption experiment illustrated that sorption of metals on  $\text{CaCO}_3$  was less reversible than OM because sorption on carbonate minerals is often dominated by strong chemical interactions. (6) Speciation and SI of metals were influenced by pH. Free metal percentage decreased as pH increased, while the percentage of carbonate and hydroxyl species increased. (7) Cadmium and Ni solutions were undersaturated with respect to most minerals, except otavite for Cd and  $\text{NiCO}_3$  (s) and  $\text{Ni(OH)}_2$  (c) for Ni at high pH range. In contrast to the Cd and Ni, the MINTEQ program demonstrated that Fe solutions were saturated with respect to all of Fe minerals at  $\text{pH} > 4$ .

## References

- Afkhami, A., Saber-Tehrani, M., & Bagheri, H. (2010). Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2, 4-dinitrophenyl-hydrazine. *Journal of Hazardous Materials*, *181*, 836–844.
- Allison, J. D., Brown, D. S., & Novo-Gradac, K. J. (1991). MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.0 User's Manual, EPA/600/3-91/021.
- Ammari, T., & Mengel, K. (2006). Total soluble Fe in soil solutions of chemically different soils. *Geoderma*, *136*, 876–885.
- Anderson, P. R., & Christensen, T. H. (1988). Distribution coefficients of Cd, Co, Ni, and Zn in soils. *Journal of Soil Science*, *39*, 15–22.
- Antoniadis, V., & Tsadilas, C. D. (2007). Sorption of cadmium, nickel, and zinc in mono- and multimetal systems. *Applied Geochemistry*, *22*, 2375–2380.
- Appel, C., & Ma, L. (2002). Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of Environmental Quality*, *31*, 581–589.
- Arnesen, A. K. M., & Singh, B. R. (1998). Plant uptake and DTPA-extractability of Cd, Cu, Ni and Zn in a Norwegian alum shale soil as affected by previous addition of dairy and pig manures and peat. *Canadian Journal of Soil Science*, *78*, 531–539.
- Baes, C. F., & Mesmer, R. E. (1976). *The Hydrolysis of Cations* (p. 489). New York: Wiley.
- Bolton, K. A., & Evans, L. J. (1996). Cadmium adsorption capacity of selected Ontario soils. *Canadian Journal of Soil Science*, *76*, 183–189.
- Bouyoucos, G. J. (1962). Hydrometer method improved for making particle size analyses of soils. *Agronomy Journal*, *54*, 464–465.
- Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, *277*, 1–18.
- Cavallaro, N., & McBride, M. B. (1978). Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal*, *42*, 550–556.
- Christensen, T. H., Lehmann, N., Jackson, T., & Holm, P. E. (1996). Cadmium and nickel distribution coefficients for sandy aquifer materials. *Journal of Contaminant Hydrology*, *24*, 75–84.
- Elliot, H. A., Liberati, M. R., & Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality*, *15*, 214–219.
- Gao, Y. Z., He, J. Z., Ling, W. T., Hu, H. Q., & Liu, F. (2003). Effects of organic acids on copper and cadmium desorption from contaminated soils. *Environment International*, *29*, 613–618.
- Garcia-Miragaya, J., & Page, A. L. (1978). Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition. *Water, Air, and Soil Pollution*, *9*, 289–299.
- Ge, Y., Murray, P., & Hendershot, W. H. (2000). Trace metal speciation and bioavailability in urban soils. *Environmental Pollution*, *107*, 137–144.
- Gerke, J. (1997). Aluminium and iron(III) species in the soil solution including organic complexes with citrate and humic substances. *Zeitschrift für Pflanzenernährung und Bodenkunde*, *160*, 427–432.
- González, A. G., Pokrovsky, O. S., Jiménez-Villacorta, F., Shirokova, L. S., Santana-Casiano, J. M., González-Dávila, M., et al. (2014). Iron adsorption onto soil and aquatic bacteria: XAS structural study. *Chemical Geology*, *372*, 32–45.
- Gray, C. W., McLaren, R. G., Roberts, A. H. C., & Condon, L. M. (1998). Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research*, *36*, 199–216.
- Han, F. X., & Singer, A. (2007). Solution chemistry of trace elements in arid zone soils. In F. X. Han (Ed.), *Biogeochemistry of trace elements in arid environments* (pp. 69–105). Springer Dordrecht: Environmental Pollution.
- Harter, R. D. (1983). Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Science Society of America Journal*, *47*, 47–51.
- Iyaka, Y. A. (2011). Nickel in soils: a review of its distribution and impacts. *Scientific Research and Essays*, *6*, 6774–6777.
- Jalali, M., & Hemati, N. (2013). Chemical fractionation of seven heavy metals (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) in selected paddy soils of Iran. *Paddy and Water Environment*, *11*, 299–309.
- Jalali, M., & Hemati Matin, N. (2015). Sorption of phosphorus in calcareous paddy soils of Iran: effects of soil/solution ratio and pH. *Environment and Earth Science*, *73*, 2047–2059.
- Jalali, M., & Moradi, F. (2013). Competitive sorption of Cd, Cu, Mn, Ni, Pb and Zn in polluted and unpolluted calcareous soils. *Environmental Monitoring and Assessment*, *185*, 8831–8846.
- Jiang, H., Li, T., Han, X., Yang, X., & He, Z. (2012). Effects of pH and low molecular weight organic acids on competitive adsorption and desorption of cadmium and lead in paddy soils. *Environmental Monitoring and Assessment*, *184*, 6325–6335.
- Karaca, A. (2004). Effect of organic wastes on the extractability of cadmium, copper, nickel, and zinc in soil. *Geoderma*, *122*, 297–303.

- Kinneburgh, D. G., Jackson, M. L., & Sayers, J. K. (1976). Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminum. *Soil Science Society of America Journal*, *40*, 796–799.
- Krishnamurti, G. S. R., Huang, P. M., & Kozak, L. M. (1999). Desorption kinetics of cadmium from soils using M ammonium nitrate and M ammonium chloride. *Communications in Soil Science and Plant Analysis*, *30*, 2785–2800.
- Lamb, D. T., Ming, H., Megharaj, M., & Naidu, R. (2009). Heavy metal (Cu, Zn, Cd and Pb) partitioning and bioaccessibility in uncontaminated and long-term contaminated soils. *Journal of Hazardous Materials*, *171*, 1150–1158.
- Lee, S. Z., Allen, H. E., Huang, C. P., Sparks, D. S., Sanders, P. F., & Peijnenburg, W. J. G. M. (1996). Predicting soil-water partition coefficients for cadmium. *Environmental Science and Technology*, *30*, 3418–3424.
- Li, Y. M., Chaney, R. L., & Schneiter, A. A. (1995). Effect of soil chloride level on cadmium concentration in sunflower kernels. *Plant and Soil*, *167*, 275–280.
- Li, X., Zhou, Q., Wei, S., Ren, W., & Sun, X. (2011). Adsorption and desorption of carbendazim and cadmium in typical soils in northeastern China as affected by temperature. *Geoderma*, *160*, 347–354.
- Lindsay, W. L. (1972). Inorganic phase equilibria of micronutrients in soils. In J. J. Mortvedt, P. M. Giordano, & W. L. Lindsay (Eds.), *Micronutrients in agriculture* (pp. 41–57). Soil Science Society of America: Madison.
- Lindsay, W. L. (1979). *Chemical Equilibrium in Soils* (p. 449). New York: Wiley.
- Loganathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2012). Cadmium sorption and desorption in soils: a review. *Critical Reviews in Environmental Science and Technology*, *42*, 489–533.
- Mahdavi, S., Jalali, M., & Afkhami, A. (2013). Heavy metals removal from aqueous solutions using TiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> nanoparticles. *Chemical Engineering Communications*, *200*, 448–470.
- Maldonado, M. T., & Price, N. M. (2001). Reduction and transport of organically bound iron by *Thalassiosira oceanica* (Bacillar-ophyceae). *Journal of Phycology*, *37*, 298–309.
- Marchi, G., Guilherme, L. R. G., Chang, A. C., Curi, N., & Guerreiro, M. C. (2006). Changes in isoelectric point as affected by anion adsorption on two Brazilian Oxisols. *Communications in Soil Science and Plant Analysis*, *37*, 1357–1366.
- Mashhady, A. S., & Rowell, D. L. (1978). Soil alkalinity. II. The effects of Na<sub>2</sub>CO<sub>3</sub> on iron and manganese supply to tomatoes. *Soil Science*, *29*, 367–372.
- McBride, M. B. (1989). Reactions controlling heavy metal solubility in soils. In B. A. Stewart (Ed.), *Advances in Soil Science* (pp. 1–56). New York: Springer.
- McBride, M. B. (1994). *Environmental Chemistry of Soils* (p. 406). Oxford Univ. Press, New York.
- McBride, M. B. (1980). Chemisorption of Cd<sup>2+</sup> on calcite surfaces. *Soil Science Society of America Journal*, *44*, 26–28.
- McGrath, S. P., Sanders, J. R., & Shabaly, M. H. (1988). The effects of soil organic matter levels on soil solution concentrations and extractabilities of manganese, zinc and copper. *Geoderma*, *42*, 177–188.
- McLaughlin, M. J., Palmer, L. T., Tiller, K. G., Beech, T. W., & Smart, M. K. (1994). Increasing soil salinity causes elevated cadmium concentrations in field-grown potato tubers. *Journal of Environmental Quality*, *23*, 1013–1018.
- Mellis, E. V., Pessoa da Cruz, M. C., & Casagrande, J. C. (2004). Nickel adsorption by soils in relation to pH, organic matter and iron oxides. *Scientia Agricola*, *61*, 190–195.
- Merdy, P., Tarchouna Gharbi, L., & Lucas, Y. (2009). Pb, Cu and Cr interactions with soil: sorption experiments and modeling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *347*, 192–199.
- Merrikhpour, H., & Jalali, M. (2013). Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. *Clean Technologies and Environmental Policy*, *15*, 303–316.
- Moharami, S., & Jalali, M. (2013). Effects of cations and anions on iron and manganese sorption and desorption capacity in calcareous soils from Iran. *Environment and Earth Science*, *68*, 847–858.
- Moral, R., Gilkes, R. J., & Jordan, M. M. (2005). Distribution of heavy metals in calcareous and non-calcareous soils in Spain. *Water, Air, and Soil Pollution*, *162*, 127–142.
- Morse, J. W. (1986). The surface chemistry of calcium carbonate minerals in natural waters: an overview. *Marine Chemistry*, *20*, 91–112.
- Naidu, R., Bolan, N. S., Kookana, R. S., & Tiller, K. G. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, *45*, 419–429.
- Naidu, R., Kookana, R. S., Sumner, M. E., Harter, R. D., & Tiller, K. G. (1997). Cadmium sorption and transport in variable charge soils: a review. *Journal of Environmental Quality*, *26*, 602–617.
- Najafi, S., & Jalali, M. (2015). Effects of organic acids on cadmium and copper sorption and desorption by two calcareous soils. *Environmental Monitoring and Assessment*, *187*, 585–595.
- Norvell, W. A., Wu, J., Hopkins, D. G., & Welch, R. M. (2000). Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. *Soil Science Society of America Journal*, *64*, 2162–2168.
- Rattan, R. K., & Deb, D. L. (1981). Self-diffusion of zinc and iron in soils as affected by pH, CaCO<sub>3</sub>, moisture, carrier and phosphorus levels. *Plant and Soil*, *63*, 377–393.
- Rowell, D. L. (1994). *Soil science: methods and applications* (p. 345). Harlow: Longman Group.
- Schulin, R., Johnson, A., & Frossard, E. (2010). Trace element-deficient soils. In P. S. Hooda (Ed.), *Trace elements in soils* (pp. 175–197). Chichester: Wiley.
- Schulthess, C. P., & Huang, C. P. (1990). Adsorption of heavy-metals by silicon and aluminum-oxide surfaces on clay-minerals. *Soil Science Society of America Journal*, *54*, 679–688.
- Seatz, L. F., & Peterson, H. B. (1964). Acid, alkaline, saline and sodic soils. In F. E. Bear (Ed.), *Chemistry of the soil* (pp. 292–319). Reinhold Publishing Corporation.
- Serrano, S., O'Day, P. A., Vlassopoulos, D., Garcia-Gonzalez, M. T., & Garrido, F. (2009). A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochimica et Cosmochimica Acta*, *73*, 543–558.
- Shaheen, S. M., Tsadilas, C. D., & Rinklebe, J. (2013). A review of the distribution coefficients of trace elements in soils: influence of sorption system, element characteristics, and soil colloidal properties. *Advances in Colloid and Interface Science*, *201–202*, 43–56.

- Smolders, E., & Mertens, J. (2013). Cadmium. In B. J. Alloway (Ed.), *Heavy metals in soils: trace metals and metalloids in soils and their bioavailability* (pp. 283–311). Springer Dordrecht: Environmental Pollution.
- Sparks, D. L. (2003). *Environmental soil chemistry* (p. 352). Academic Press, New York.
- Sposito, G. (1989). *The chemistry of soils* (p. 277). New York: Oxford University Press.
- Sposito, G., & Schindler, P. W. (1986). Reactions at the soil colloid-soil solution interface. In L. Landner (Ed.), *Speciation of metals in water, sediment and soil systems* (pp. 683–699). Springer Verlag, Berlin.
- Sposito, G., Lund, J., & Chang, A. C. (1982). Trace metal chemistry in arid zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Science Society of America Journal*, *46*, 260–264.
- Stevenson, F. J. (1982). *Humus chemistry: genesis, composition, reactions* (p. 443). New York: John Wiley & Sons.
- Suavé, S., McBride, M., & Hendershot, W. (1998). Soil solution speciation of lead(II): effects of organic matter and pH. *Soil Science Society of America Journal*, *62*, 618–621.
- Suavé, S., Hendershot, W., & Allen, H. E. (2000). Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology*, *34*, 1125–1131.
- Sunda, W., & Huntsman, S. A. (1997). Interrelated influence of iron, light, and cell size on marine phytoplankton growth. *Nature*, *390*, 391–392.
- Tack, F. M. G. (2010). Trace elements: general soil chemistry, principles and processes. In P. S. Hooda (Ed.), *Trace elements in soils* (pp. 9–39). Chichester: Wiley.
- Tiller, K. G., Gerth, J., & Briimmer, G. (1984). The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. *Geoderma*, *34*, 17–35.
- Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M. R., Lofts, S., Hill, M. T. R., et al. (2003). The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environmental Pollution*, *125*, 213–225.
- Tye, A. M., Young, S., Crout, N. M. J., Zhang, H., Preston, S., Zhao, F. J., et al. (2004). Speciation and solubility of Cu, Ni and Pb in contaminated soils. *European Journal of Soil Science*, *55*, 579–590.
- Uren, N. C. (1992). Forms, reactions, and availability of nickel in soils. In D. L. Sparks (Ed.), *Advances in agronomy* (pp. 141–203). New York: Academic Press.
- Usman, A. R. A. (2008). The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt. *Geoderma*, *144*, 334–343.
- Vert, G., Grotz, N., Dédaldéchamp, F., Gaymard, F., Guerinot, M. L., Briat, J. F., et al. (2002). IRT1, an Arabidopsis transporter essential for iron uptake from the soil and for plant growth. *The Plant Cell*, *14*, 1223–1233.
- Violante, A., Krishnamurti, G. S. R., & Pigna, M. (2008). Factors affecting the sorption–desorption of trace elements in soil environments. In A. Violante, P. M. Huang, & G. M. Gadd (Eds.), *Biophysico-chemical processes of heavy metals and metalloids in soil environments* (pp. 215–261). Inc: John Wiley & Sons.
- Wagner, G. J. (1993). Accumulation of cadmium in crop plants and its consequences to human health. *Advances in Agronomy*, *51*, 173–212.
- Wang, Y. J., Zhou, D. M., Luo, X. S., Sun, R. J., & Chen, H. M. (2004). Cadmium adsorption in montmorillonite as affected by glyphosate. *Journal of Environmental Sciences (China)*, *16*, 881–884.
- Yang, J. Y., Yang, X. E., He, Z. L., Li, T. Q., Shentu, J. L., & Stoffella, P. J. (2006). Effects of pH, organic acids, and inorganic ions on lead desorption from soils. *Environmental Pollution*, *143*, 9–15.
- Yang, Y., Zhang, F. S., Li, H. F., & Jiang, R. F. (2009). Accumulation of cadmium in the edible parts of six vegetable species grown in Cd-contaminated soils. *Journal of Environmental Management*, *90*, 1117–1122.
- Yin, Y., Allen, H. E., Li, Y., Huang, C. P., & Sanders, P. F. (1996). Adsorption of mercury (II) by soil: effects of pH, chloride, and organic matter. *Journal of Environmental Quality*, *25*, 837–844.
- Zachara, J. M., Cowan, C. E., & Resch, C. T. (1991). Sorption of divalent metals on calcite. *Geochimica et Cosmochimica Acta*, *55*, 1549–1562.