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# Influence of Organo-Metal Interactions on Regeneration of Exhausted Clay Mineral Sorbents in Soil Columns Loaded with Heavy Metals



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## ABSTRACT

Natural clay minerals can play an important role in crude remediation of wastewater polluted with the heavy metals (HMs) Cu, Zn and Ni. The presence and timing of addition of natural dissolved organic matter (DOM) have a significant effect on the HM removal by clay mineral sorbents. However, the influence of the presence of DOM on the remediation of the used clay mineral sorbents once saturated with HMs is largely unknown. To resolve this, clay mineral-rich soil column of varying composition, loaded (i) with Cu, Zn and Ni only, (ii) first with DOM followed by Cu, Zn and Ni, or (iii) with DOM, Cu, Zn and Ni simultaneously, was used in a set of desorption experiments. The soil columns were leached with 0.001 mol L<sup>-1</sup> CaCl<sub>2</sub> dissolved in water as control eluent and 0.001 mol L<sup>-1</sup> CaCl<sub>2</sub> dissolved in DOM as treatment eluent. During the preceding loading phase of the sorbent, the timing of DOM addition (sequential or concurrent with HMs) was found to have a significant influence on the subsequent removal of the HMs. In particular when the column was loaded with DOM and HMs simultaneously, largely irreversible co-precipitation took place. Our results indicate that the regeneration potential of clay mineral sorbents in wastewater treatment will be significantly reduced when the treated water is rich in DOM. In contrast, in manured agricultural fields (where HMs enter together with DOM), HM mobility will be lower than expected from interaction dynamics of HMs and clay minerals.

**Key Words:** dissolved organic matter, heavy metal mobility, remediation, timing of addition, wastewater treatment

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The amount of wastewater contaminated with heavy metals (HMs) worldwide increases continuously due to the expansion of industrial activities, and wastewater contamination has been subject of much research as a result of the related public health hazards (Qin *et al.*, 2004; Fu and Wang, 2011). Adsorption technology using natural clay minerals is seen as an important remediation measure, particularly in developing countries where more sophisticated techniques are usually not widely available (Ikhsan *et al.*, 2005; Gu *et al.*, 2010; de Almeida Neto *et al.*, 2012; Refaeey *et al.*, 2014). Clay minerals and/or hydroxides (Mn and Fe hydroxides) are adsorbents that are both abundant and cheap (Moreno-Castilla and Rivera-Utrilla, 2001; Al-Qunaibit *et al.*, 2005; Colombani *et al.*, 2015). Given their high specific surface area (SSA) and cation exchange capacity (CEC), the mobility and bioavailability of HMs can be substantially reduced by interac-

tions with clay minerals, hydroxides and dissolved organic matter (DOM) (Stahl and James, 1991; Kalbitz and Wennrich, 1998; Antoniadis *et al.*, 2007; Refaeey *et al.*, 2014, 2015, 2017; Colombani *et al.*, 2015).

Due to cost-efficiency, such wastewater treatment approaches using clay mineral sorbents would ideally use a continuous system in which sorbent materials can be used in multiple cycles of metal sorption and desorption (Mehta and Gaur, 2005; Alpana *et al.*, 2012; Unuabonah *et al.*, 2013). Since desorption often controls the environmental fate of most contaminants and treatment feasibility, insights in the recovery potential of HMs from clay minerals used in wastewater treatment are essential (Mustafa *et al.*, 2004; Hu and Shipley, 2012). After the adsorbents are exhausted, they are either to be discarded or, preferably, recovered for reuse. Spent sorbents should be released into the environment only after removal of the adsorbed HMs

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to avoid secondary pollution to soil and groundwater systems (Karathanasis, 1999; Tzou *et al.*, 2007; Lata *et al.*, 2015). In spite of the importance of regeneration of adsorption materials for wastewater treatment, this has received surprisingly little research attention (Glover *et al.*, 2002; Covelo *et al.*, 2004; Feng *et al.*, 2012; Lata *et al.*, 2015). In particular, knowledge is lacking about the influence of DOM in HM-containing wastewater on the subsequent removal potential of the HMs once adsorbed. In our previous work it was shown that not only the presence of DOM, but also the timing of its addition prior to or simultaneously with HM addition, have great influence on the removal efficiency of Zn, Ni and Cu through adsorption on clay minerals (Refaey *et al.*, 2017).

The DOM contains a variety of reactive functional groups, such as carboxyl, phenol, amine or thiol, acting as ligands with various affinities for HMs (Hur and Kim, 2009). Metals are often strongly bound to DOM; therefore, the complexation of metals by DOM strongly alters the fate and toxicity of these metals in the environment (Leenheer and Croué, 2003; Kozyatnyk *et al.*, 2016). The toxic HMs such as Cu, Zn and Ni were found to primarily bind to the acidic fractions in the DOM due to the presence of negatively charged hydroxyl and carboxyl groups (Jeong *et al.*, 2007; Witt *et al.*, 2009). Laborda *et al.* (2008) reported that the contribution of the humic acid (HA) fraction to leaching of Cu is lower than that of the fulvic acid (FA) fraction, whereas the contribution of the FA fraction for both Ni and Zn was higher (Zn  $\gg$  Ni) than that of HA. In addition, HA and FA show different mobilities, because FA is soluble at any pH and is, hence, highly mobile in the environment, whereas HA is insoluble at acid pH (Laborda *et al.*, 2009). Understanding the mechanisms controlling the interactions of HMs with both minerals and DOM is therefore essential to get insights into mobility of HMs (Arshad *et al.*, 2008; Cecchi *et al.*, 2008; Refaey *et al.*, 2017).

Specifically, our previous work (Refaey *et al.*, 2014, 2017) confirmed that Cu was mostly retained to clay minerals and hydroxides through inner-sphere complexes, whereas both Zn and Ni were bound predominantly through outer-sphere complexes (electrostatic interactions). Furthermore, the addition of DOM and its timing of addition had a significant effect on the removal of HMs from aqueous solution. The concurrent addition of DOM and HMs to the sorbent materials resulted in a large enhancement of the affinity and adsorption capacity for all tested HMs, particularly for Cu because of its high affinity toward DOM (Lair *et al.*, 2007). In contrast, sequential addition of DOM to

the sorbents (prior to HMs) resulted in decreased affinity and adsorption capacity for all tested HMs due to coating or blocking the binding sites on the clay minerals and hydroxides in sorbent materials (Refaey *et al.*, 2014). Therefore, both the presence of DOM and timing of its addition should be considered in design of wastewater cleanup strategies based on adsorption on clay minerals. However, it is unclear how the timing of DOM addition may influence desorption behaviors of Cu, Zn and Ni in column regeneration upon saturation with HMs.

Therefore, the objective of this study was to investigate the role of the presence and timing of addition of DOM during loading of clay mineral in wastewater treatment columns on the subsequent removal of HMs from the columns after use. For this the columns of varying clay mineralogical composition, adopted in our previous study, were used after their saturation with HMs and under the various DOM addition scenarios previously tested. Two desorption reagents were investigated based on the assumption that such reagents should be cost-effective, eco-friendly and must not damage the sorbent materials (Das, 2010). The majority of metals are adsorbed *via* ion exchange reactions and are in competition for adsorption sites with other cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ . Therefore, the use of these competing cations for enhancing HM desorption deserves attention (Lu and Xu, 2009). Many authors have proposed the use of natural salts such as  $\text{CaCl}_2$  as an extraction reagent because of its low cost, relatively low environmental impact, and efficiency for the regeneration of HMs without destroying the sorbent matrix (Reed *et al.*, 1996; Houba *et al.*, 2000; Makino *et al.*, 2006; Meers *et al.*, 2007). In addition, this extraction procedure with  $\text{CaCl}_2$  is used in the Dutch legislation for the assessment of nutrients and HMs in soils (Pueyo *et al.*, 2004). Furthermore,  $\text{Ca}^{2+}$  is the most common divalent cation in soil and groundwater, it is nontoxic at high concentrations, and there is no drinking water standard set for this element (Wang *et al.*, 1997). In addition, complexing agents such as organic compounds have also been investigated for enhancing desorption of HMs (Tan *et al.*, 1994; Schwab *et al.*, 2007; Wuana *et al.*, 2010). As a result, the  $\text{CaCl}_2$  solutions in water (control eluent) and DOM (treatment eluent) were chosen as reagents for column regeneration.

## MATERIALS AND METHODS

### *Experimental materials*

In our previous study (Refaey *et al.*, 2017), soil sa-

mples from southern Limburg, The Netherlands and mixed solutions of chloride salts of Cu, Ni, and Zn ( $25 \text{ mg L}^{-1}$ ) were used in the column adsorption experiments. In the adsorption step, the original soil was amended with smectite ( $100 \text{ g kg}^{-1}$ ), goethite ( $10 \text{ g kg}^{-1}$ ) and birnessite ( $10 \text{ g kg}^{-1}$ ) because of their prominent role in regulating the binding affinity of Cu, Ni, and Zn (Refaey *et al.*, 2014, 2015). The mineral amendments were used to create 5 different soil compositions with the non-amended soil as a control, as described in the previous study (Refaey *et al.*, 2017). Each prepared soil was mixed with 5.0 g of sand (50–70 mesh particle size, Sigma-Aldrich, USA) to increase the hydrological conductivity of the soil once packed in the column, so the final weight of each prepared soil was 10.0 g (Refaey *et al.*, 2017). The DOM used in both the current and our previous study was prepared by aqueous extraction from organic matter (soil with natural manure) following the method described by Refaey *et al.* (2014, 2017).

#### Experimental setup

The preparation of soil columns ( $12 \text{ cm} \times 2.5 \text{ cm}$ ) for the adsorption step was described in detail in our previous study (Refaey *et al.*, 2017). Afterwards, the same soil column was used to study column regeneration in the present study. To prevent preferential flow paths and for precise control of the flow rate, the eluent solutions were pumped upwards against gravity by means of peristaltic pumps (Minipuls 3, Gilson, USA) with a flow rate of  $0.333 \text{ mL min}^{-1}$ . The desorption experiments were conducted on the sorbents loaded with the tested metals through 3 adsorption scenarios (A, B and C) as described in Table I.

Two  $\text{CaCl}_2$  eluents were prepared. The first eluent (control) was  $0.001 \text{ mol L}^{-1}$   $\text{CaCl}_2$  dissolved in deionized water, and the second eluent (treatment) was  $0.001 \text{ mol L}^{-1}$   $\text{CaCl}_2$  dissolved in DOM. The eluent solutions were adjusted to pH 6 before starting the experiments by adding appropriate amounts of 0.1 and  $0.01 \text{ mol L}^{-1}$  NaOH to avoid precipitation of DOM. The adsorption experiments in our previous study (Re-

faey *et al.*, 2017) were carried out in quadruplicate for each tested sorbent, and therefore in the present study for each sorbent, the first 2 duplicates were regenerated with the control eluent and the 2 others with the treatment eluent. Desorption of metal-loaded sorbents was initiated by continuous flow of eluent solution at a flow rate of  $0.333 \text{ mL min}^{-1}$ . A constant head of reagent solution was maintained in the column throughout the desorption period (up to continuous 18 h). Eluted fractions were collected at intervals of 45 min from 60 columns (20 columns for each scenario). The concentrations of HMs and DOM in each eluted fraction were determined with an inductively coupled plasma optical emission spectrometer (Optima 3000 XL, PerkinElmer, USA) and a TOC analyzer (TOC-VCPH, Shimadzu, Japan), respectively.

#### Desorption parameters

To evaluate the regeneration process, the desorbed amounts ( $M_d$ ) of the tested metals were calculated by Eq. 1 (Voleski *et al.*, 2003; Lodeiro *et al.*, 2006) from the desorption curve, which is equivalent to the breakthrough curve in the adsorption step.

$$M_d = \frac{Q}{M_s} \int_{t=0}^{t=t_e} C_d dt \quad (1)$$

where  $C_d$  ( $\text{mg L}^{-1}$ ) is the metal concentration after the elution process at time  $t$ ;  $t_e$  (min) is the time required for total elution of HMs in column;  $M_d$  is calculated from the numerical integration of the regeneration curves from  $t = 0$  to  $t = t_e$ ; and the integrated part was calculated by the area below the elution curve ( $C_d$  vs  $t$ ) multiplied by the flow rate ( $Q$ ) and soil mass ( $M_s$ ). The computer program ORIGIN was used to calculate the area under the curve by numerical integration.

The result of desorption was described by the desorption efficiency ( $E$ , %), obtained by dividing the desorbed amount of metal ( $M_d$ ) by the amount of metal bound to the sorbent in the previous adsorption experiments ( $M_a$ ) as follow:

$$E = M_d/M_a \times 100\% \quad (2)$$

TABLE I

Eluents and soil column pretreatment for desorption experiments

Eluents	Column pretreatment		
	Scenario A	Scenario B	Scenario C
$\text{CaCl}_2$ only (control eluent), $\text{CaCl}_2$ and dissolved organic matter (DOM) (treatment eluent)	Sorbents loaded with heavy metals (HMs) only	Sorbents loaded with DOM first and then HMs	Sorbents loaded with DOM and HMs simultaneously

## RESULTS

*Regeneration of heavy metal-loaded sorbents using control eluent*

The desorption efficiency ( $E$ ) for the HMs followed the sequence of Ni > Zn > Cu in scenario A and Zn > Ni > Cu in scenarios B and C (Table II). The recovery of Cu from the sorbents in scenarios A and B was quite similar except for the soil-smectite sorbent that showed higher Cu removal in scenario A compared to B (Fig. 1). Furthermore, a larger variation in  $E$  among the tested sorbents was recorded for Cu in scenario A (19%–64%) compared to scenario B (26%–37%). For both Zn and Ni, the  $E$  values were higher in scenario A (37%–81% for Zn and 41%–89% for Ni) compared to scenario B (39%–57% for Zn and 37%–53% for Ni). In scenario C, the  $E$  values for Cu (2%–5%), Zn (11%–18%) and Ni (8%–17%) were always much lower than those in scenarios A and B (Table II, Fig. 1).

*Regeneration of heavy metal-loaded sorbents using treatment eluent*

The  $E$  values for the HMs followed the order of Cu > Ni > Zn in scenarios A and B while of Cu > Zn > Ni in scenario C (Table III). When using the treatment eluent, the  $E$  value was higher under scenario B than under scenario A for all the tested metals and sorbents (Table III). Furthermore, a large increase in desorption was achieved for only Cu under scenario B using the treatment eluent (69%–78%), compared with the control eluent (26%–37%) (Fig. 1). For both Zn and

Ni, mostly a reduction of desorption was found under scenario A (47%–53% for Zn and 53%–60% for Ni), sometimes combined with an enhancement of desorption under scenario B (54%–69% for Zn and 68%–74% for Ni).

The recoveries of the tested HMs were always much lower under scenario C than under scenario A or B (Fig. 1). For Cu, while still remaining lower than those under scenarios A and B, the  $E$  value under scenario C was significantly enhanced by flushing with the treatment eluent (15%–25%) as compared to the control eluent (2%–5%) (Fig. 1). Only small differences in  $E$  of both Zn and Ni were found upon flushing with control (11%–18% for Zn and 8%–17% for Ni) or treatment eluent (12%–19% for Zn and 12%–15% for Ni).

The released HMs from the sorbents varied based on the type of scenario. The metals adsorbed onto different sorbents in scenario A (0.82–1.22, 0.72–1.10, and 0.59–0.80 mg g<sup>-1</sup> sorbent for Cu, Zn, and Ni, respectively) (Refaey *et al.*, 2017) were released more using the control and treatment eluents (0.326–1.021, 0.358–1.015, and 0.300–0.819 mg g<sup>-1</sup> sorbent for Cu, Zn, and Ni, respectively), comparing to scenario B (0.348–0.900, 0.318–0.540, and 0.262–0.517 mg g<sup>-1</sup> sorbent for Cu, Zn, and Ni, respectively). In scenario C, the released HMs were very low (0.086–0.799, 0.255–0.353, and 0.177–0.285 mg g<sup>-1</sup> sorbent for Cu, Zn, and Ni, respectively) (Tables I and II, Fig. 1).

*Effect of sorbent composition on desorption of HMs*

Upon flushing with the control eluent, hydroxide-

TABLE II

Removal and desorption efficiencies ( $E$ ) of heavy metals from loaded clay mineral sorbents in soil columns using 0.001 mol L<sup>-1</sup> CaCl<sub>2</sub> dissolved in deionized water as eluent under 3 adsorption scenarios A, B and C

Sorbent	Heavy metal	Scenario A		Scenario B		Scenario C	
		Removal	$E$	Removal	$E$	Removal	$E$
		mg g <sup>-1</sup> sorbent	%	mg g <sup>-1</sup> sorbent	%	mg g <sup>-1</sup> sorbent	%
Soil (control)	Cu	1.201	35.4	0.366	29.1	0.121	3.5
	Zn	0.970	49.1	0.382	47.0	0.255	14.4
	Ni	0.770	50.2	0.319	40.8	0.177	11.6
Soil-smectite	Cu	0.578	63.7	0.343	34.3	0.158	2.2
	Zn	0.618	62.6	0.318	50.7	0.327	10.6
	Ni	0.411	82.0	0.262	42.6	0.272	9.2
Soil-goethite	Cu	0.326	31.7	0.384	34.0	0.207	4.5
	Zn	0.762	70.6	0.375	52.3	0.361	18.3
	Ni	0.641	89.1	0.311	45.8	0.278	16.7
Soil-birnessite	Cu	0.432	19.3	0.348	25.6	0.111	1.8
	Zn	0.494	37.4	0.336	39.1	0.293	12.6
	Ni	0.405	40.8	0.284	36.7	0.217	10.9
Soil-smectite-hydroxides	Cu	0.351	48.0	0.386	36.8	0.086	1.6
	Zn	0.358	80.5	0.367	57.2	0.269	11.4
	Ni	0.300	75.8	0.328	53.4	0.180	8.1

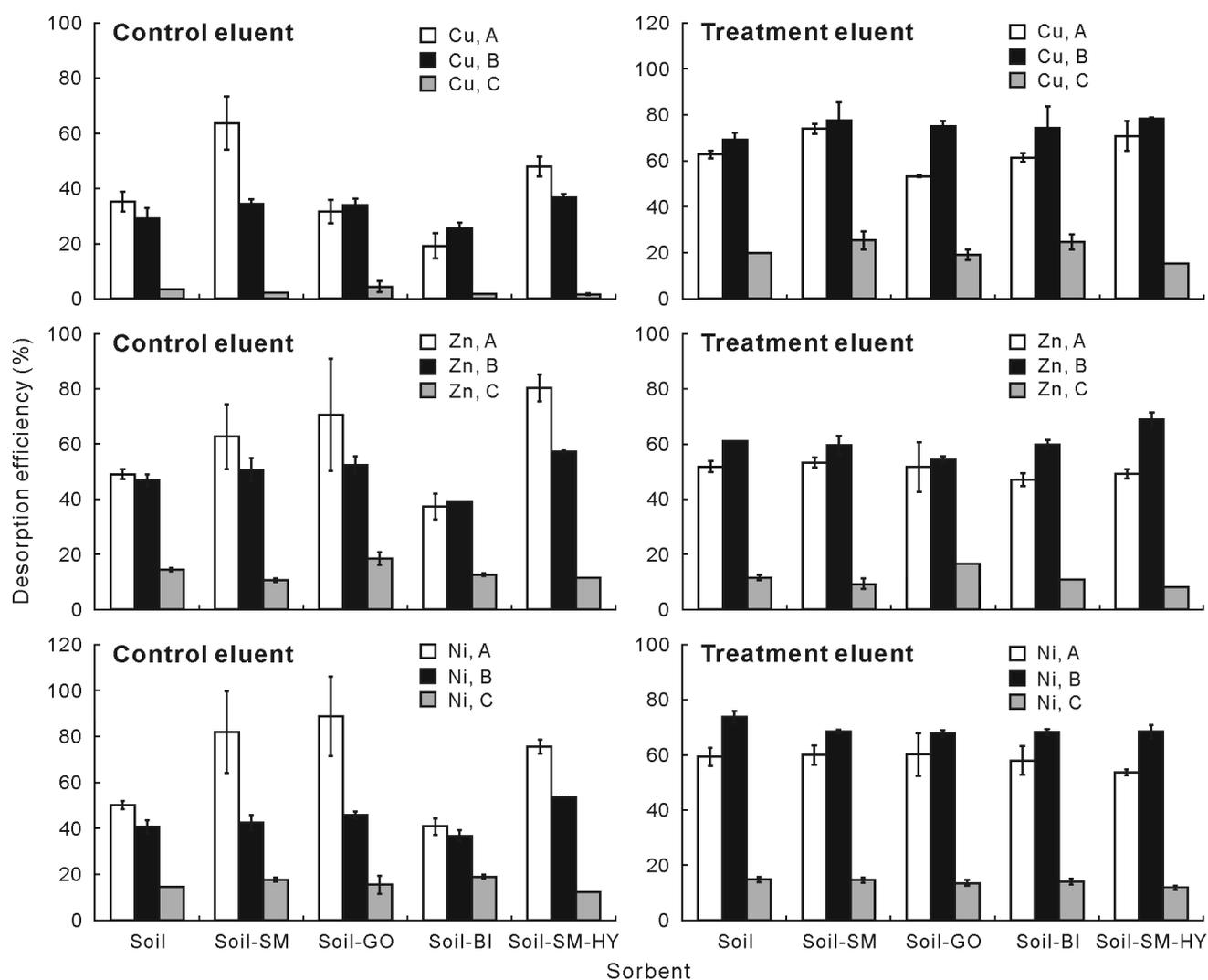


Fig. 1 Desorption efficiencies of Cu, Zn and Ni from loaded clay mineral sorbents in soil columns using  $0.001 \text{ mol L}^{-1}$   $\text{CaCl}_2$  dissolved in deionized water and in dissolved organic matter as eluents (control eluent and treatment eluent, respectively) under 3 adsorption scenarios A, B and C. Vertical bars indicate standard errors of the means ( $n = 2$ ). SM = smectite; GO = goethite; BI = birnessite; HY = hydroxides.

rich sorbents (soil-birnessite and soil-goethite) showed a low release of Cu, while the  $E$  values were quite similar under scenarios A and B (Table II). Upon flushing with the treatment eluent, the release of Cu was remarkably enhanced (Table III), in particular from soil-goethite. For both Zn and Ni, their release from soil-goethite with the control eluent was lower in scenario B than in scenario A (Table II). Also, the soil-smectite showed a larger release for Cu, Zn and Ni in scenario A than in scenario B (Tables II and III).

## DISCUSSION

### *Regeneration of heavy metal-loaded sorbents using control eluent*

The desorption efficiency of HMs by  $\text{CaCl}_2$  may be

considered as an expression of the strength of bonds and mobility of the HMs (Kowalkowski *et al.*, 2010). Since Cu sorption depends mainly on covalent interactions (inner-sphere complex) with the soil constituents (Kandpal *et al.*, 2005; Kowalkowski *et al.*, 2010; Refaey *et al.*, 2014, 2017), as expected Cu proved rather resistant to exchange with  $\text{Ca}^{2+}$  in the present study. In contrast, both Zn and Ni, which are predominantly retained by exchange reactions (outer-sphere complexes), were effectively removed by the  $\text{CaCl}_2$  solution as a result of cation exchange with abundant  $\text{Ca}^{2+}$ .

The absence of DOM in the metal-loaded sorbents under scenario A led to much higher recovery of HMs from smectite-amended sorbents (soil-smectite and soil-smectite-hydroxides) than from the other soil compositions tested (Fig. 1). This can be explained by

TABLE III

Removal and desorption efficiencies ( $E$ ) of heavy metals from loaded clay mineral sorbents in soil columns using 0.001 mol L<sup>-1</sup> CaCl<sub>2</sub> dissolved in dissolved organic matter as eluent under 3 adsorption scenarios A, B and C

Sorbent	Heavy metal	Scenario A		Scenario B		Scenario C	
		Removal	$E$	Removal	$E$	Removal	$E$
		mg g <sup>-1</sup> sorbent	%	mg g <sup>-1</sup> sorbent	%	mg g <sup>-1</sup> sorbent	%
Soil (control)	Cu	1.021	62.7	0.802	69.0	0.717	19.9
	Zn	1.015	51.9	0.540	61.1	0.312	14.6
	Ni	0.819	59.3	0.517	73.9	0.240	14.7
Soil-smectite	Cu	0.946	73.9	0.713	77.6	0.650	25.3
	Zn	0.960	53.3	0.440	59.6	0.328	17.6
	Ni	0.766	59.9	0.388	68.5	0.253	14.4
Soil-goethite	Cu	0.569	53.2	0.650	75.2	0.590	19.1
	Zn	0.490	51.7	0.363	54.4	0.353	15.3
	Ni	0.443	60.1	0.352	67.8	0.285	13.4
Soil-birnessite	Cu	0.662	61.3	0.900	74.3	0.799	24.6
	Zn	0.417	47.1	0.433	59.9	0.350	19.0
	Ni	0.377	58.0	0.406	68.4	0.236	13.9
Soil-smectite-hydroxides	Cu	0.701	70.8	0.875	78.2	0.702	15.2
	Zn	0.421	49.2	0.456	68.9	0.325	12.1
	Ni	0.378	53.7	0.400	68.4	0.245	11.7

the fact that smectite-rich soil is composed of aluminosilicate minerals, which favored cation exchange of metal ions during the adsorption process (Atanassova, 1995; Abat *et al.*, 2012; Refaey *et al.*, 2015). Interestingly, soil-birnessite showed the lowest release of Cu, Zn and Ni among the tested sorbents, indicating that the previously observed large affinity of all tested metals for the birnessite-rich sorbent (Refaey *et al.*, 2017) contributed at the same time to the slowing down of metal recovery, which is in line with other studies (Khan *et al.*, 2005; Wang *et al.*, 2010). The overall recovery sequence of the tested metals under scenario A was Ni > Zn > Cu, which agrees with Halmous *et al.* (2015) and our previous study (Refaey *et al.*, 2017), where a higher affinity of Zn and Cu was found compared to Ni for adsorption on smectite and hydroxides.

Owing to the stability of Cu, Zn and Ni complexes with previously adsorbed organic matter, reduction in their recoveries was recorded under scenario B compared to under scenario A, in particular for Cu. As Cu forms the most stable complexes with organic matter, the competitive exchange of Cu with Ca<sup>2+</sup> was weak (Stevenson, 1994; Bradl, 2004). Nevertheless, the  $E$  value for Cu was higher than those for both Zn and Ni (Fig. 1). Moreover, the higher electronegativity of Cu and Ni and their tendency to form stronger bonds with organic matter, compared with Zn, led to a decrease in their  $E$  values (Halmos *et al.*, 2015).

#### *Regeneration of heavy metal-loaded sorbents using treatment eluent*

Compared to Zn and Ni, Cu is much more suscep-

tible to specific binding to organic matter owing to its previously mentioned preference for inner-sphere complexation (Karlsson *et al.*, 2006; Lair *et al.*, 2007). As a result, using the treatment eluent containing DOM enhanced Cu desorption in all 3 scenarios as compared to the control eluent that did not contain DOM. The enhancement in Cu recovery was particularly strong in scenario B, most likely because in this scenario, where the columns were loaded first by DOM and then by Cu, Cu was to a large extent bound to DOM adsorbed on the mineral phase rather than to the mineral phase itself. As a result, removal of this fraction consisted of simple partitioning between binding of Cu to DOM adsorbed on the mineral phase and DOM present in the treatment eluent. In addition, the binding affinity of Ca<sup>2+</sup> to DOM is much weaker than that of Cu to DOM, which also explains the lower desorption efficiency of Cu compared to Zn and Ni (Ma *et al.*, 1999; Halmos *et al.*, 2015).

In contrast, the desorption efficiency of both Ni and Zn was reduced in scenario A and remarkably enhanced in scenario B when the treatment eluent was used instead of the control eluent (Fig. 1). The most likely explanation is that part of Ca<sup>2+</sup> in the treatment eluent was bound to DOM in solution, leaving less free Ca<sup>2+</sup> to displace Zn<sup>2+</sup> and Ni<sup>2+</sup> adsorbed on the columns under scenario A. The enhanced desorption of Zn and Ni in scenario B when the using treatment eluent suggests again that there is partitioning between the DOM adsorbed on the mineral phase and the DOM in the treatment eluent. Given the outer-sphere bonding character of Ni and Zn, such

association with DOM on the mineral phase was much likely through non-specific binding mechanisms (Bradl, 2004).

Based on our findings, which agree with Halmos *et al.* (2015), two different metal leaching sequences ( $\text{Ni} > \text{Zn} \gg \text{Cu}$  and  $\text{Cu} > \text{Ni} > \text{Zn}$ ) were specified using the control and treatment eluents in scenario A (data not shown). Therefore, it can be stated that the high affinity of Cu and Zn compared to Ni for the mineral phase in the absence of DOM is responsible for the high recovery of Ni followed by Zn and then Cu, while in the presence of DOM (treatment eluent) the high affinity for DOM and electronegativity of both Cu and Ni contribute to the high recoveries of these two metals compared to that of Zn. This also explains the metal leaching sequence ( $\text{Zn} > \text{Ni} > \text{Cu}$ ) in scenarios B and C using the control eluent (data not shown), showing high recovery of Zn compared to Ni and Cu.

#### *Effect of prior addition of DOM on desorption of Cu, Zn and Ni*

The present study confirms a clear effect of the timing of addition of DOM during the loading of the columns on the desorption of Cu, Zn and Ni from various sorbents. The effect of loading with DOM and subsequently with HMs (scenario B) before flushing with the control or treatment eluents is described in the previous paragraphs. Metal desorption from the columns where HMs and DOM were added concurrently (scenario C) was markedly different; the *E* values were much lower using both the control and treatment eluents for all metals and from all the tested sorbents (Fig. 1).

Apparently, the concurrent addition of HMs and DOM led to predominantly irreversible immobilization of loaded metals. This suggests that immobilization does not take place predominantly *via* adsorption of the metal cations to clay minerals or adsorbed DOM as in scenario B, but most likely through co-precipitation of DOM-HM complexes in the column as also hinted in our previous study (Refaey *et al.*, 2017). Organic ligands can form chelate complexes with HMs, causing them to be tightly adsorbed to the soil constituents (Alloway, 1995). With co-precipitation as the dominant immobilization mechanism, flushing with  $\text{CaCl}_2$  dissolved in water or in DOM is inefficient in removing metals as only little metal is available for desorption. These results once more underpin the crucial, yet to our knowledge never previously considered, role of the timing of HM and DOM addition on HM mobility in soils. This has a significant impact on risk assessment with respect to the mobility of HMs in

soils and connected groundwater systems, indicating that such mobility may be greatly reduced in scenarios where HMs are introduced simultaneously with DOM, *e.g.*, through application of HM-rich manure, but not in systems where they are introduced sequentially.

#### *Performance of examined eluents and potential reusability of sorbent material*

The control eluent was highly effective in recovering both Zn and Ni from the mineral phase in scenario A and the maximum removal was up to 80% and 90%, respectively. In contrast, the treatment eluent containing DOM was only effective in scenario B where the maximum removal of Zn and Ni was 70% and 75%, respectively. No adequate removal of Zn or Ni could be obtained under scenario C (concurrent saturation of the column with DOM and HMs), with the maximum removal of 19% for Zn and 17% for Ni. For Cu, the recovering process was effective only when using the treatment eluent in scenarios A and B, yielding a maximum removal of 75% and 80%, respectively. Again, the removal efficiency of Cu under scenario C was inadequate with a maximum of 25%. These results imply that regeneration of clay mineral columns used in treatment of HM-polluted wastewater through flushing with  $\text{CaCl}_2$  solutions with or without DOM may be a viable technique, but only in cases where the wastewater itself does not simultaneously contain HMs and DOM.

## CONCLUSIONS

In the absence of loaded DOM (scenario A), Ni and Zn that are predominantly bound to the mineral phase (outer-sphere complexes) showed substantial removal of up to 89% and 81%, respectively, through simple cation exchange with  $\text{Ca}^{2+}$ . However, when using DOM in the eluent a reduction in desorption of Ni and Zn was found because of binding of part of exchangeable  $\text{Ca}^{2+}$  to DOM. In contrast, Cu was less readily recovered by  $\text{Ca}^{2+}$  (maximum 64%) due to its inner-sphere complexation with the sorbent, but its desorption efficiency was remarkably enhanced to up to 74% when eluted with DOM because of its inner-sphere complexation with functional groups on DOM. The previously loaded HMs together with DOM showed substantial differences in desorption process depending on whether HM loading had taken place concurrently with (scenario C) or sequentially to DOM loading (scenario B). When the soil columns were first loaded with DOM followed by HMs, the highest removal efficiency (up to 69% for Zn, 74% for Ni and 78% for Cu)

was achieved using DOM in the eluent. This indicates a partitioning between HMs bound to DOM adsorbed on the solid phase and to DOM in solution. However, when the columns were loaded with HMs and DOM simultaneously prior to desorption, the removal efficiencies were rather low for all metals (2%–25% for Cu, 11%–19% for Zn and 8%–17% for Ni, depending on clay mineral composition) regardless of whether desorption treatment consisted of CaCl<sub>2</sub> in water or in DOM. This indicates that immobilization of heavy metals in the column loaded with HMs and DOM simultaneously takes place to a large extent through irreversible co-precipitation rather than adsorption. For the purpose of regeneration of clay minerals used in wastewater treatment, the present study indicates that this will be significantly reduced when the treated wastewater is rich in DOM. For natural soil systems, our results suggest that when HMs enter a soil together with DOM, *e.g.*, through application of HM-rich manure in agricultural fields, the mobility of HMs will be much lower than expected from interaction of HMs and clay minerals alone. In general, Cu-loaded soils are more susceptible to remobilization of Cu when DOM-rich water infiltrates, whereas Ni- and Zn-loaded soils are more susceptible to remobilization when cation-rich water infiltrates. However, in circumstances where precipitation plays a role (scenario C), additional measures, for instance acidification to re-dissolve precipitates, would be needed.

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