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Comparison of organic materials for the passive treatment of synthetic neutral mine drainage contaminated by nickel: Short- and medium-term batch experiments

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Abstract

This paper addresses the comparison of various low-cost organic materials for the passive treatment of circum-neutral pH contaminated mine water. First, the effectiveness of five organic materials to remove Ni from a contaminated neutral drainage (CND) was compared in short-term batch experiments (24 h) at various pH values. Second, based on results of the short-term experiments, two substrates (brown algae and sawdust) were eliminated and three (horticultural peat, compost, wood ash) were compared along with a new substrate (field-collected surface peat) in medium-term (56 days) batch experiments to treat CND. In these experiments, calcite was added to peat samples and all substrates performed equally well, sequestering over 97 % of the Ni. Chemical extractions revealed that Ni was more strongly bound to the horticultural peat-calcite (HD-peat-calcite) residue than to the field-collected peat-calcite (LT-peat-calcite) residue. Compost, because of its higher density, was identified as the most promising candidate for sorption-based fixed-bed column experiments.

Nevertheless, wood ash should not be discarded as its alkaline properties favor nickel removal.

1. Introduction

At mine sites, contaminated discharge water can be generated when water and air circulate through waste rock piles. Contaminated neutral drainage (CND) refers to an effluent with pH values ranging between 6 and 9 and with metal concentrations that exceed local regulatory discharge limits (Nordstrom et al. 2015). This type of drainage can occur when the acidity resulting from the oxidation of sulfide minerals is buffered by the presence of carbonate or silicate minerals in the gangue rock.

During mining operations, metal contaminated effluents are typically treated by active methods in water treatment plants. Ultimately, these techniques which are not acceptable for final rehabilitation of closed or abandoned mining sites in Quebec, Canada (MERN 2017), need to be replaced by passive methods, especially after cessation of operations. The implementation of gravity feed passive reactors is considered an efficient technology to treat mining effluents (Kefeni et al. 2017; Neculita et al. 2007). Metal capture mechanisms in these reactors are varied and can include sorption onto solid substrates as well as precipitation or co-precipitation of mineral phases such as (oxy)hydroxides, carbonates or sulfides (Neculita et al. 2008; Sheoran and Sheoran 2006; Skousen et al. 2017). The sequestration mechanisms in these reactors depend on many inter-related parameters such as the nature of the solid substrate in the reactor, the dissolved constituents that this substrate will generate, the Eh and pH conditions, the hydraulic residence time (HRT) and the composition of the incoming contaminated drainage. Generally, long HRTs, on the order of days, are

needed to achieve bacterial sulfate reduction and sulfide precipitation in passive reactors designed for the treatment of acid mine drainage (AMD) and these passive bioreactors require voluminous treatment systems (Neculita et al. 2007; Skousen et al. 2017). Alternatively, less voluminous short HRT systems, designed to promote sorption or precipitation of oxidized species, may provide economical solutions to treat the typically lower metal and sulfate concentrations of CND, especially if low-cost or free materials such as waste materials or natural organic substrates are used. In these reactors, contact times of a few minutes to a few hours between the CND and the substrate may suffice to achieve the desired remediation level (Mayes et al. 2009; Nuttall and Younger 2000; Trumm and Pope 2015; Warrender et al. 2011). The main metal(loid) contaminants of CND are Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, U, Zn, As, Sb, and Se (Calugaru et al. 2018). Their concentrations in CND are variable and mostly contingent on the mineralogy of each particular mine site. Apart from their distinct but relatively low potentially toxic metal content, CND is typically characterized by high concentrations of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) that originate from the dissolution of the gangue minerals.

Different approaches have been tested for the treatment of various types of CND. For Fe and Mn-rich effluents, methods that oxidize and/or increase the pH of the effluent to enhance Fe and Mn (oxy)hydroxide precipitation are generally used (de Repentigny et al. 2018; Sapsford and Williams 2009; Sung et al. 2015). Other metals in these effluents may also be removed by adsorption onto these newly formed (oxy)hydroxide phases (Trumm and Pope 2015). For low-Fe effluents, two approaches are commonly applied

for the sequestration of divalent metals. These can either be removed by adsorption onto adsorbent materials or by increasing the pH of the effluent to promote their precipitation or co-precipitation as carbonates or hydroxides (Mayes et al. 2009; Nuttall and Younger 2000; Warrender et al. 2011). In some cases, both mechanisms can occur simultaneously such as when alkaline sorbent materials like wood or fly ash (Calugaru et al. 2017; Warrender et al. 2011) or mixed materials such as pelletized hydrous ferric oxide in Portland cement are used (Mayes et al. 2009).

The financial cost of transporting materials to remote mining sites can be substantial and thus substrates in the present study were selected for their sorption properties and potential local availability to eastern Canadian mining sites. In the first part of the study, the Ni sorption capacities of five organic materials were compared by conducting short-term (24h) batch experiments in synthetic CND under varying pH conditions (pH 6, 7, 8, and natural pH of the substrate). The objectives were to evaluate the effect of pH and solution composition on Ni uptake and to present the criteria used for the selection of materials for the subsequent medium-term batch experiments. For this evaluation, the results of a previous study (Richard et al. 2020) in which the material's sorption kinetics and isotherms had been evaluated at fixed pH (7) and in the absence of competing ions were used, and geochemical modeling was performed. In the second part of the study, four substrates (horticultural peat, field-collected peat, compost, and wood ash) were compared in medium-term (56 days) batch experiments. The objectives were to evaluate their Ni sequestration efficiency and uptake kinetics, verify whether their degradation would affect their Ni retention capacity, and assess the potential

mobility of Ni in the spent materials. Selection criteria for future long-term testing in column experiments (not presented here) were also discussed.

2. Materials and methods

2.1 Synthetic CND preparation and equipment

The composition of the CND used in this study was inspired from a Lac Tio mine effluent, a low-Fe Ni-contaminated drainage originating from the waste piles of a massive ilmenite deposit located near Havre-Saint-Pierre (Québec, Canada)(Plante et al. 2010). The field-measured pH of this effluent is generally between 6.5 and 7.8 and Ni concentrations vary, occasionally exceeding the local provincial regulation (0.5 mg/L and 1 mg/L mean monthly and maximum acceptable concentrations, respectively) if not treated. The synthetic CND for the short- (CND_{ST}) and medium-term (CND_{MT}) batch experiments were prepared based on the composition of a grab mine effluent sample (Table 1 presents the initial compositions for these solutions). The only difference between the protocols followed to make the two synthetic CND solutions was that CND_{ST} did not initially contain Ni whereas CND_{MT} did. This is because the pH needed to be adjusted in CND_{ST} prior to the addition of Ni for short-term experiments in order to prevent, as much as possible, the pH adjustment phase and associated reactions from interfering with Ni sorption. The initial Ni concentration used for short- and medium-term batch experiments (7.45 mg/L) was much higher than measured in the field and it was chosen as a worst-case scenario as well as to ensure analytical detection for all

measurements. As trace metals preferentially fill specific adsorption sites over the major cations (McLean and Bledsoe 1992), the Zn, Co and Mn concentrations in the synthetic CNDs were proportionally increased along with the Ni concentration to maintain their relative roles as competitive ions. The synthetic CNDs were prepared in deionized water with sulfate and chloride salts of ACS grade or better, filtered through a 0.45 μm Millipore MCE membrane, and stored at room temperature in a closed 4 L HDPE container for no more than two weeks prior to the experiments. Four separate batches of stock solution were used in short-term experiments and one was used in medium-term experiments. Stock solutions were analyzed regularly throughout their period of use.

pH measurements were carried out with a pH meter (model Orion Star A211 benchtop, ThermoScientific) using a combination glass electrode (model Orion 9156BNWP, ThermoScientific). The electrode was calibrated against three NIST-traceable buffer solutions of pH 4.01, 7.00, and 10.00 at 25 °C. The total alkalinity (endpoint pH 4.5) was measured by colorimetry using a dilute sulfuric acid solution and a bromocresol green-methyl red indicator (LaMotte 4533-DR; MDL of 4 mg/L eq. $CaCO_3$). The cation concentrations (Table 1) were determined by flame atomic absorption spectrometry (AAS; Perkin-Elmer AAnalyst-200). Calibration curves were built by sequential dilution of AAS standard (~1000 ppm) solutions (Perkin-Elmer) and the reproducibility of the measurements was better than 2 %, based on replicate analyses of these solutions. The anion concentrations (Table 1) were measured by different methods during short- and medium-term batch experiments. During the short-term experiments, sulfate

concentrations were determined with a Jenway 6300 spectrophotometer using the turbidimetric method 4500-SO_4^{2-} (APHA 2005), whereas chloride ion concentrations were quantified using Hach QuanTab® test strips (MDL 30 mg/L, uncertainty 13 mg/L). In the medium-term batch experiments, anion concentrations were determined by ion chromatography (model Thermo Scientific ICS 5000 AS-DP DIONEX). Calibration curves were prepared using diluted mono- and multi-element(s) standard solutions (Hach and Thermo Fisher) and anions were detected by conductivity after being separated in an As18-4 micron column (Thermo Scientific (DIONEX)) with a KOH eluent. The reproducibility of the measurements was better than 2 %, based on replicate analyses of a CND_{MT} solution.

Table 1 Composition of an unfiltered field sample and the synthetic CND solutions used in short- and medium-term batch experiments

Parameter	Lac Tio mine field sample[1]		Synthetic CND				Source
	Value	DL	CND$_{ST}$[3]	CND$_{MT}$[4]	DL		
Ca (mg/L)	251	0.02	240 ± 8	244 ± 15	-		CaSO$_4$ · 2H$_2$O
Mg (mg/L)	64	0.01	65 ± 3	67± 3	-		MgSO$_4$ · 7H$_2$O
Na (mg/L)	66	0.035	61 ± 11	76 ± 3	-		NaCl, NaNO$_3$, Na$_2$SO$_4$
K (mg/L)	4.6	0.2	4.4 ± 0.6	4.2 ± 0.5	-		K$_2$SO$_4$
Ni (mg/L)	2.29	0.001	0	7.69±0.4	0.01		NiSO$_4$
Zn (mg/L)	0.55	0.007	1.78 ± 0.04	1.74 ±	0.01		ZnSO$_4$ · 7H$_2$O
Mn (mg/L)	0.37	0.001	0.91 ± 0.20	1.08 ±	0.01		MnSO$_4$ · H$_2$O
Co (mg/L)	0.59	0.0003	2.29 ± 0.35	2.15 ±	0.01		CoCl$_2$ · 6H$_2$O
					DL$_{ST}$[5]	DL$_{MT}$	
SO$_4$$^{2-}$ (mg/L)	897	0.5	901 ± 18	960 ± 1	1.3	0.2	Ca, Mg, Na, K, Zn and Mn sulfates
Cl$^-$ (mg/L)	84	1	77 ± 4	89 ± 2	30	0.5	NaCl
NO$_3$$^-$ (mg/L)	1.92	0.02	-	1.8	-	0.2	NaNO$_3$
pH	7.25	-[2]	7.17 ± 0.10	7.26	-		NaHCO$_3$, CO$_2$
Alk.(mg/L CaCO$_3$)	46	-	12 ± 4	12 ± 4	-		-

[1] Measurements were done at Exova Group Laboratory. Anions were measured by ion chromatography according to MA. 300 – Ions 1.3 and MA. 303-Anions, cations by ICP-MS according to MA. 200-Mét 1.2 and alkalinity by titration to 4.5 according to method MA 315 – Alc-Acl 1.0 (CEAEQ 2019). [2] Hyphens indicate that the values are not available. [3] Results are expressed as mean ± standard deviation using n = 9 (ions) and n=17 (pH). [4] Results are expressed as mean ± standard deviation using n = 3 (cations) and n=2 (SO$_4$$^{2-}$ and Cl$^-$). [5] Anions were determined by different methods in CND$_{ST}$ and CND$_{MT}$, see text for details.

2.2 Organic substrates for short- and medium-term batch experiments

The five substrates used in the short-term experiments were: 1) cold-water brown algae, *Ascophyllum nodosum* (ASCO-PURE kelp), provided by Organic Ocean Inc. (Rimouski, Quebec), sieved to less than 5 mm; 2) horticultural sphagnum peat moss (HD-peat), purchased from a local retailer (Home Depot, Montreal), sieved to less than 5 mm; 3) compost, produced from green wastes by the City of Montreal, sieved to less

than 5 mm; 4) maple sawdust (particles < 5 mm), provided by P.W.I. Industries (Saint-Hyacinthe, Quebec); 5) wood ash (a mixture of bottom and fly ash, particles < 5 mm), provided by Wood Ash Industries (Kirkland Lake, Ontario). Three of these substrates (compost, wood ash, and HD-peat) were used in the medium-term batch experiment, along with a second field-collected surface sphagnum peat moss (LT-peat). The LT-peat was collected with a shovel near the Lac Tio mine site and manually crumbled. LT-peat fibers measured less than 1 cm (see Online Resource 1 – Fig. S3). All substrates were air-died and kept at room temperature in plastic containers.

The physico-chemical characteristics of the six materials used in this study are presented in Table 2. The water content of each solid substrate was determined prior to the adsorption experiments by drying 5-10 g of substrate at 60 °C until constant weight was obtained. The pH of a slurry of each substrate (2g substrate: 100mL deionized water) was measured after mixing thoroughly and letting stand for 1 h. The specific surface areas (SSA) of the substrates were measured with a Micromeritics Gemini III 2375 surface analyzer using the N_2-BET method PE2 AM-05 (Brunauer et al. 1938). The q_{max} parameter, an empirical value linked to the maximal sorption capacity of substrates under field relevant conditions, was obtained by fitting the Langmuir equation to the results of a short-term (20 h) Ni isotherm experiment in 0.05M $NaNO_3$ at pH 7 (Richard et al. 2020). Initial Ni concentrations in this experiment were: 0.6, 7, 15, 29, 59 and 103 mg/L. The total carbon (C_{TOT}) as well as the total organic and graphitic carbon (C_{org+g}) content of the substrates were measured by combustion at 1400 °C with an induction furnace (model CS744, LECO Corporation) according to method MA. 310-CS 1.0 (CEAEQ

2013). The reproducibility of the measurements was better than 2 %, based on replicate

analyses of a standard reference material (MRG1) and the detection limit was 0.1 %. The

C_{org+g} sample was prepared by dissolving the solid inorganic carbon for at least one hour

in a 50 % v/v HCl solution, filtering and analyzing the residual solid. Dissolved organic

carbon (DOC) was analyzed on filtered (0.45 μm) extracts of slurries (20 g substrate (wet

weight): 200 mL deionized water) shaken for 2 h with a rotary agitator (150 RPM) at

room temperature. The DOC was determined at 680 °C using a DOHRMAN model DC-

190 TOC analyzer, according to Standard Method 5310 B (APHA 2005). The

reproducibility of the measurements was better than 2 %, based on replicate analyses of

diluted TOC standard solutions (Hach), and the detection limit was 1 mg/L.

Table 2 Physico-chemical characteristics of organic materials used in sorption
experiments

	Water content (% w/w)	pH	SSA (m^2/g)	q_{max} (mg/g)	C_{TOT} (% w/w dry wt.)	C_{org+g} (% w/w dry wt.)	DOC – water extract (mg/L)
Algae[1]	8.9 ± 1.6	5.47 ± 0.21	0.17	-[3]	34.9 ± 0.1	26.1 ± 0.4	5680 ± 160
Sawdust[1]	5.0 ± 0.5	4.68 ± 0.36	0.91	3.8 ± 0.9	50.1 ± 0.4	49.3 ± 1.6	669 ± 6
Wood ash[1]	2.8 ± 0.7	9.32 ± 0.37	45.9	3.9 ± 1.4	19.9 ± 2.2	18.6 ± 2.3	6.36 ± 0.81
Compost[1]	3.9 ± 0.3	7.30 ± 0.25	3.24	8.8 ± 2.8	17.3 ± 4.3	15.2 ± 0.6	79.5 ± 1.9
HD-peat[1]	11.4 ± 0.7	5.06 ± 0.39	1.43	22 ± 9	53.4 ± 0.0	53.3 ± 1.0	132 ± 7
LT-peat[2]	11.2 ± 0.4	3.94 ± 0.27	1.52	-[4]	47.3 ± 1.0	43.5 ± 1.1	172 ± 7

[1]Results are expressed as mean ± standard deviation using n = 4 (water content), n=3 (pH, CEC), n=2 (C_{TOT}, $Corg_{TOT}$), n=6 (DOC). [2]Results are expressed as mean ± standard deviation using n= 3 (pH, CEC) and n=2 (water content, C_{TOT}, C_{org+g}, DOC). [3]q_{max} parameter was not obtained with algae results as they did not form a curvilinear trend. [4] Not tested.

2.3 Short-term batch experiment

For short-term experiments, 2 g (dry weight) of substrate and 200 mL of CND_{ST} were stirred (150 RPM) at room temperature (22.4 ± 1.2°C) on a MaxQ-2000 orbital shaker (ThermoScientific). Experiments were conducted in duplicate reactors (500 mL Erlenmeyers) and flask openings were loosely covered with aluminum foil to limit evaporation. During the first 24-hour pH adjustment period, pH was either allowed to drift or adjusted to values of 6.0 ± 0.2, 7.0 ± 0.2 or 8.0 ± 0.2 using dilute H_2SO_4 and NaOH solutions. In total, eighteen experiments were conducted using thirty six reactors (see online resource 1 for details – Table S1, Fig. S1). After the pH adjustment period, of the substrate with the CND_{ST}, Ni sorption assessment was initiated by adding 0.145 mL of a 27.1 g/L (0.175 M) $NiSO_4$ solution to each reactor to obtain an initial dissolved Ni concentration of 7.45 mg/L (127 µM). At various time intervals over the next 24-hour period, nine 6mL aliquots of the slurry were collected (see online resource 1 for details – Fig. S1). The samples were immediately filtered through 0.45µm PVDF syringe filters, stored at 4 °C and analyzed for Ni within 14 days.

2.4 Medium-term batch experiments

For medium-term experiments, 3 g (dry weight) of substrate and 300 mL of CND_{MT} were stirred (150 RPM) at room temperature (21.4 ± 1.0 °C). These experimental conditions provided sufficient solution for analysis while maintaining the same solid: solution ratio as the one used in short-term batch experiments. The solids in HD-peat and LT-peat reactors (500 mL Erlenmeyers) were amended with 0.6 g of calcium carbonate (ACS

reagent grade) to raise their pH to circum-neutral values. Each experiment was conducted in duplicate reactors and flask openings were sealed by plastic foam stoppers covered with aluminum foil to limit evaporation. A third reactor (sacrificial triplicate reactor) was prepared and stirred in the same manner and sampled at 21 days to measure the parameters used in geochemical modeling. At this sampling time, a steady-state was expected to have been reached with regards to most parameters. In total, four experiments were conducted using twelve reactors (see online resource 1 – Table S1 for details). The first two duplicate reactors were sampled by withdrawing eight 12 mL aliquots of the slurry at intervals of 2 to 14 days over 56 days (see online resource 1 –Fig. S1 for details), a duration chosen to verify whether the degradation of the substrates would affect their Ni retention capacity over a longer time period. The samples were immediately filtered through 0.45 μm PVDF syringe filters and divided into sub-samples for Ni, sulfate, DOC and chemical oxygen demand (COD) analyses. The COD was determined within a few hours of sampling using a Hach, model DR6000 spectrophotometer, according to standard method 5220 D (APHA 2005). The reproducibility of the measurements was 3 %, based on replicate analyses of diluted standard solutions (Hach), and the detection limit was 3 mg/L. The Ni, sulfate and DOC samples were stored at 4 °C and analyzed within one week (Ni, SO_4^{2-}) or three weeks (DOC). The sacrificial triplicate reactors were sampled by withdrawing 80 mL aliquots of the liquid. The samples were immediately filtered through 0.45 μm PVDF syringe filters and divided into sub-samples in order to measure alkalinity, anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, F^-, Br^-) and dissolved metal concentrations. Alkalinity was measured immediately

whereas other samples were stored at 4 °C and analyzed within one week. Dissolved metals were measured at Maxaam Analytics Inc. laboratories by ICP-MS according to method MA.200-Mét. 1.2 (CEAEQ 2019). The pH and oxidation-reduction potential (ORP) were measured directly in all reactors at t = 24 h and at each sampling time. The ORP was measured using a double-junction Pt-tip Ag/AgCl electrode (model Cole-Parmer GH-59001-77) and potentiometer (model Orion Star A211 benchtop, ThermoScientific). The electrode response was calibrated with an ORP standard solution (Orion, ThermoScientific) and ORP readings are reported in millivolts (mV) with respect to the Standard Hydrogen Electrode (Eh). At the end of the batch experiment, 150 mL of the liquid was decanted from each reactor and the solid and remaining liquid were transferred to a 50 mL polypropylene tube and centrifuged at 10000 x g for 10 minutes (Heraeus Megafuge 8 ThermoScientific). The remaining liquid was removed from the tube and the solids were used in subsequent Ni mobility experiments. The concentrations, q_t (mg g^{-1}), and percentages of Ni sequestered by the solid at each sampling point were calculated using Eq.1 and Eq. 2:

$$q_t = \frac{[Ni]_{diss_0} \times V_0 - [Ni]_{diss_t} \times V_t}{m} \tag{1}$$

$$\% \ sequestered = \frac{[Ni]_{diss_0} \times V_0 - [Ni]_{diss_t} \times V_t}{[Ni]_{diss_0} \times V_0} \times 100 \tag{2}$$

where V_o, V_t, are the volumes of liquid (L) in the reactor at the start of the experiment (time = 0) and at each sampling point (time = t) and m is the mass of the solid (g).

$[Ni]_{diss_0}$ and $[Ni]_{diss_t}$ are the dissolved Ni concentrations (mg/L) at time = 0 (7.45 mg/L) and time = t.

2.5 Chemical extractions following sequestration on solid substrates and precipitates

The potential mobility of Ni sequestered on the substrates was evaluated immediately after the medium-term batch experiments by applying 1) a sequential extraction procedure (SEP) on the reacted solids from one of the duplicate batch reactors (R1) and 2) a synthetic precipitation leaching procedure (SPLP) on the reacted solids from the other batch reactor (R2). The wet solid from each reactor was divided in three equal parts of approximately 1 g (dry weight) and placed in pre-weighted centrifuge tubes (polypropylene copolymer tubes for the SEP and polypropylene tubes for the SPLP). One tube (C) from each set was dried at 60 °C until constant weight was obtained to determine the water content of the solid while the other two tubes (A & B) were used as duplicates during the experimental procedures. For the SPLP, method 1312 (U.S. EPA 1994) was applied. Briefly, 20 mL of a pH 4.2 dilute (60:40) H_2SO_4-HNO_3 solution was added to the tubes and they were shaken for 18h at on a wrist-action shaker (Boekel Scientific, model 401000). Tubes were then centrifuged at 10000 x g for 10 minutes and the supernatant extracting solutions were removed, filtered through 0.45 μm PVDF syringe filters and analyzed for their Ni content. The five-step SEP used in this study (Zagury et al. 1997) is based on the procedure devised by Tessier et al. (1979) but uses a different digestion method for the residual metal fraction. In this procedure, the operationally-defined fractions, extraction times, temperatures and solutions are: (F1)

soluble and exchangeable (1 h, 21 °C, 8 mL of 0.5 M $MgCl_2$, pH 7), (F2) carbonate bound and specifically adsorbed (5 h, 21 °C, 8 mL of 1 M NaOAc, pH 5), (F3) reducible or bound to Fe-Mn oxides (6 h, 96 °C, 20 mL of 0.04 M $NH_2OH·HCl$ in 25 % (v/v) HOAc), (F4) oxidizable or bound to organic matter (5 h, 85 °C, 20 mL of H_2O_2-HNO_3,NH_4OAc, pH 2), and (F5) residual fraction (HNO_3, HF, $HClO_4$). Between each of the successive extractions, solids and liquids were separated by centrifugation. Once the supernatant solution was removed, the solid residue was rinsed once with 8 mL of deionized water, shaken manually for 30 seconds and centrifuged again. After centrifugation, the extracting and rinsing solutions were filtered through 0.45 μm PVDF syringe filters and analyzed by AAS for their Ni content. To determine the residual metal fraction (F5), the solid residue was transferred to a Teflon beaker and digested according to method 3030 I. (APHA 1998).

2.6 Geochemical modeling

Equilibrium speciation calculations were performed using the freeware VMINTEQ version 3.1 and the associated database (Gustafsson 2019). The VMINTEQ thermodynamic database is a revised version of the original USEPA MINTEQA2 database (Allison et al. 2011) that contains updated and expanded data from the NIST Critical Stability Constant database (ver. 7). Calculations were performed for open system conditions (pCO_2 = 38.5 Pa, Eh = 560 mV) and the binding of metal ions to dissolved organic matter was modeled using the NICA-Donnan formulation with default settings. First, we modeled the effect of pH on Ni speciation in the synthetic CND_{ST} and CND_{MT} at

22.4 °C using the data from Table 1. For these models, the Ni concentration were 7.45 mg/L (127 µmol/L) for the CND_{ST} solution and 7.69 mg/L (131 µmol/L) for the CND_{MT} solution). Second, we calculated the saturation indices in the medium-term batch reactor solutions using the geochemical measurements obtained at t = 21 days in the sacrificial triplicate reactors (see model input details in Online Resource 1 - Table S2). For all models, the charge imbalance was lower than 5 %, indicating a good overall quality of the water chemistry analyses.

2.7 Spontaneous solid precipitation following pH adjustment of the experimental solutions

According to the equilibrium speciation model, experimental solutions are oversaturated or become oversaturated with respect to a number of solid phases (e.g., $NiCO_{3(s)}$, calcite, $Co_3O_{4(s)}$, etc.) as the pH of the synthetic CND is increased. To verify the validity of the speciation model calculations and confirm that solids precipitate as well as sequester Ni from the experimental solutions, five centrifuge tubes, each containing 40 mL of the synthetic CND_{ST}, were adjusted to pH values between 7 and 11 using dilute H_2SO_4 and NaOH solutions. After pH adjustment, the tubes were amended with 27 µL of 27.1 g/L (0.175 M) $NiSO_4$, in the absence of substrate, to obtain an initial dissolved Ni concentration of 6.93 mg/L (118 µmol /L). The tubes were then closed and shaken manually. Tube caps were loosened and tubes were left to stand at room temperature (22.4 ± 1.2 °C) for 48 h. After this time, the pH was measured and samples were filtered

through 0.45 μm PVDF syringe filters, stored at 4 °C and analyzed within 14 days by AAS

for Ni, Co and Mn.

3. Results

3.1 Spontaneous precipitation following pH adjustment of the experimental solutions

According to VMINTEQ equilibrium model, at pH values below 7.38, all Ni species in the

open-system modeling of the CND_{ST} are dissolved, and the main dissolved species are

Ni^{2+} and $NiSO_4°_{(aq)}$ (Fig. 1). At pH values above 7.38, the solution is oversaturated with a

Ni carbonate phase ($NiCO_{3(s)}$, Ksp = $10^{-11.2}$). At pH values above 7.88, the solution is

oversaturated with respect to calcite. Dissolved Ni, Co and Mn concentrations, after a

48h equilibration period following pH adjustment of the synthetic CND_{ST}, are presented

in Fig. 2. The dashed lines represent calcite saturation for a fixed calcium concentration

of 240 mg/L (5990 μmol/L), and $NiCO_{3(s)}$ saturation for a fixed Ni concentration of $[Ni]_{tot}$

= 7.45 mg/L (127 μmol/L). In the lower pH samples (6.94 and 7.66), the concentrations

of all three metals were relatively constant and within one standard deviation of the

mean value typically measured in the synthetic CND_{ST} (Table 1). The concentrations of

all three metals decreased significantly in the pH 8.09 sample and fell below their

respective detection limits at higher pHs when a greenish-white precipitate could be

observed. According to the model, the CND_{ST} solution is oversaturated with respect to

$Co_3O_{4(s)}$ above pH 6.23, with respect to a variety of Mn oxides above pH 6.97 and with

respect to hydrozincite above pH 7.73. Co and Mn precipitates presumably did not form

from the CND$_{ST}$ and CND$_{MT}$ stock solutions, as their solution concentrations remained constant over periods of several weeks. In the adjusted pH 7.66 sample, NiCO$_{3(s)}$ presumably did not form as Ni concentrations were equivalent to the ones measured in the pH 6.94 sample. At pH above 8, the precipitation of calcite could be responsible for the removal of these metals from the CND solutions, as they can be adsorbed to or co-precipitated with this mineral (Belova et al. 2014; Kitano et al. 1976; Zachara et al. 1991; Zachara et al. 1988). If closed system conditions (expected in fixed-bed reactors) had been used to model the CND$_{ST}$ solution instead of the actual open system conditions, oversaturation with respect to calcite would take place at pH above 8.31.
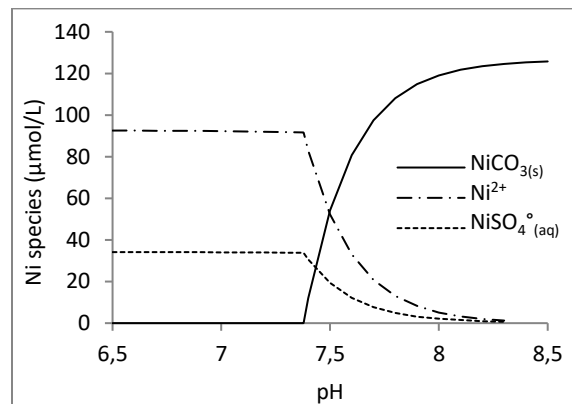
Fig. 1 Modeled Ni speciation in an open CND$_{ST}$ system with [Ni]$_{tot}$ = 7.45 mg/L or 127 µmol/L. Species with concentrations below 1 µmol/L are not presented.
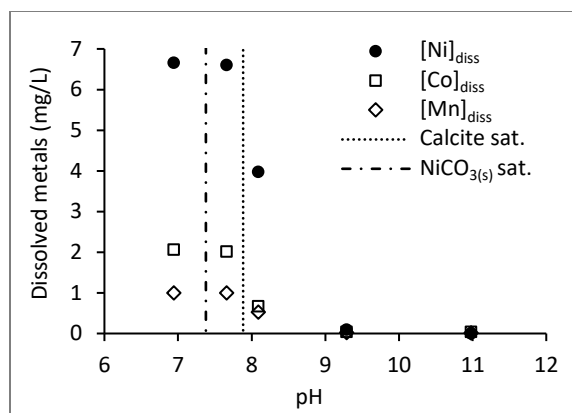
Fig. 2 Metal concentrations following pH adjustment of the CND_{ST} experimental solution. Vertical dotted lines represent $NiCO_{3(s)}$ saturation for a fixed $[Ni]_{tot}$ = 7.45 mg/L or 127 µmol/L and calcite saturation for a fixed $[Ca]$ = 240 mg/L or 5990 µmol/L.

3.2 Short-term batch experiments

During short-term experiments (Fig. 3), the dissolved Ni concentrations decreased rapidly before either stabilizing (HD-peat, algae and lower pH sawdust experiments) or adopting a much lower rate of sequestration (compost, wood ash and higher pH sawdust experiments). For all materials, Ni removal increased with pH. Fig. 4 shows the removal of Ni by the different materials under the pH conditions tested after about 6 h of equilibration, when most of the Ni sequestration had taken place and the pH was close to the targeted values (6.0, 7.0, 8.0). The temporal evolution of solution pH is presented in Online Resource 1 – Fig.S2. In the wood ash reactor, the dissolution of reactive Ca, Na and K oxides, hydroxides and carbonates may have increased the pH of the CND solution (Demeyer et al. 2001; Ohno 1992; Ulery et al. 1993). While little is

know about the exact mineralogy of the wood ash, X-ray diffraction results from a previous study (Genty et al. 2012) have shown that calcite was significantly present in materials supplied by Wood Ash Industries.
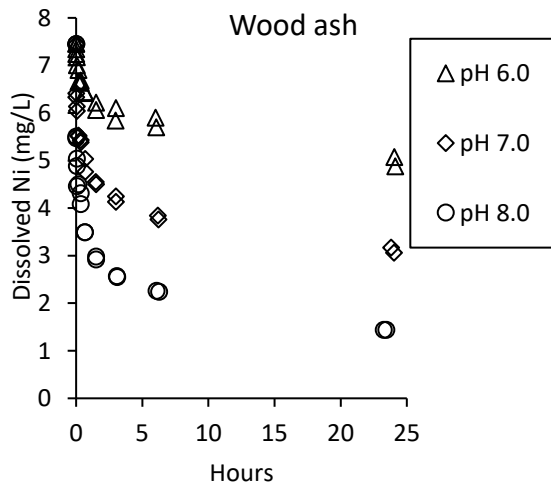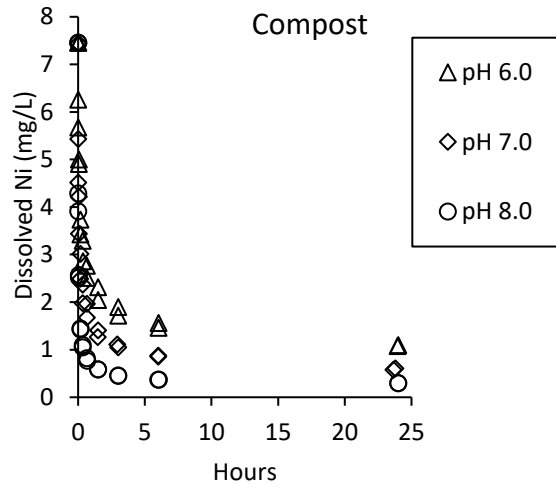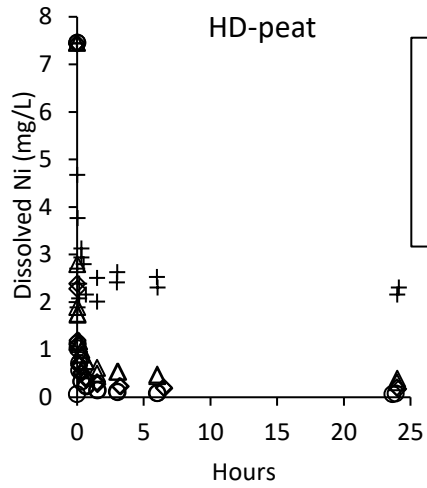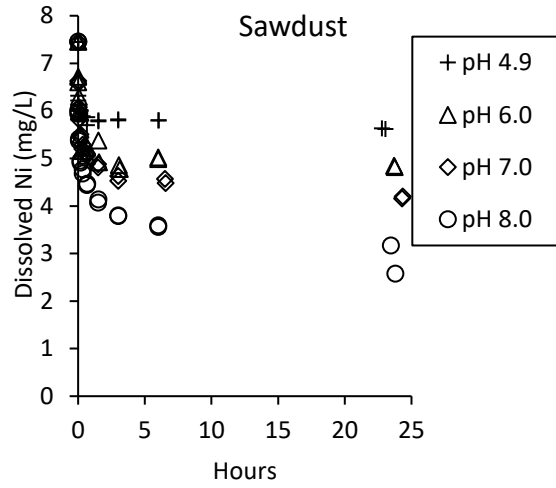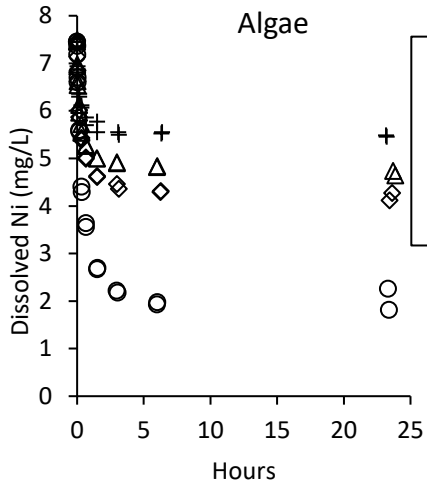
Fig. 3 Dissolved Ni concentrations as a function of time in presence of each organic material tested. Initial Ni concentration was 7.45 mg/L in all reactors and duplicate results are presented for each pH tested.
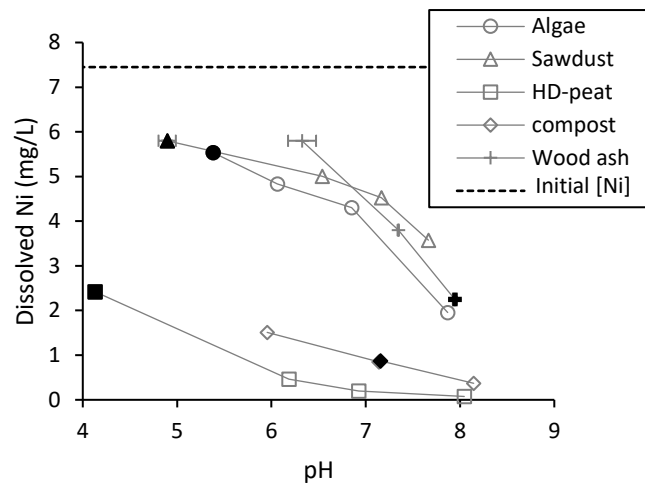

Fig. 4 Comparison of dissolved Ni concentrations as a function of pH measured during short-term experiments (t ≈ 6 h). Results are presented as average values from duplicate reactors, with error bars representing one standard deviation from the mean. Full symbols represent results of experiments conducted at the natural pH of the substrates. Dashed line represents the initial Ni concentration.

3.3 Medium-term batch experiments

The results of medium-term batch experiments (Fig. 5) are presented as average parameter values from duplicate (Ni, SO_4^{2-}, DOC, COD) or triplicate (Eh, pH) reactors, with error bars representing one standard deviation from the mean. Eh and pH values varied over the first two to seven days of the experiment. During this period, Eh values increased slightly (by up to 100 mV) in all reactors before settling at around 550 ± 15 mV. Over the same time period, pH increased in the calcite-amended peat (peat-calcite) reactors, slightly decreased in the wood ash reactors and remained stable in the compost reactors. After one week, the pH of the wood ash, compost and peat-calcite reactor slurries stabilized, and values of 8.06 ± 0.15 (wood ash), 7.19 ± 0.14 (compost), and 7.52 ± 0.11 (HD- and LT-peat-calcite) were recorded from this point on. In all reactors, dissolved Ni was effectively removed from the solutions while sulfate concentrations were nearly stable throughout the experiments. The initial DOC concentrations of the wood ash, compost, LT-peat-calcite and HD-peat-calcite slurries were, respectively, 9 mg/L, 25 mg/L, 23 mg/L and 37 mg/L. The DOC concentrations increased steadily in all reactors but to different extents, increasing in the following order: wood ash < compost < LT-peat < HD-peat whereas the COD remained relatively constant in compost and wood ash reactors, and increased in the first two weeks in the peat-calcite reactors.
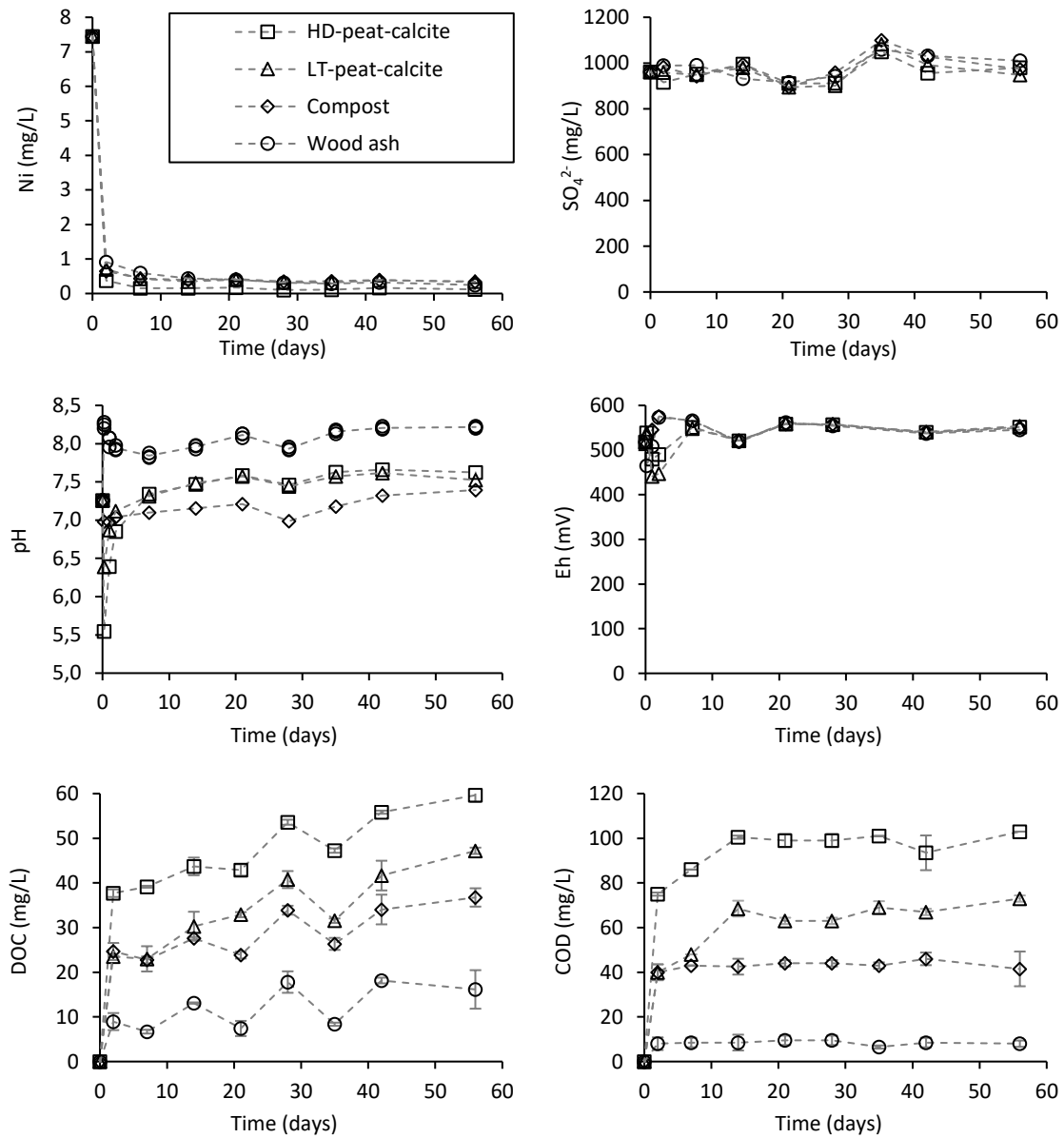
Fig. 5 Temporal evolution of physico-chemical parameters during medium-term batch experiments

3.4 Geochemical modeling of medium-term batch reactor solutions

Geochemical modeling was conducted in order to compare solutions in the different medium-term batch reactors. When experiments begin, the mineral and organic components of the substrate may dissolve in the CND_{MT} solution. Solutes released will either remain in solution, increasing its ionic strength, or be removed by adsorption, precipitation or co-precipitation. The sampling of batch reactors at t = 21 days provides information on the composition of the slurries once the solids and liquids have equilibrated and most parameters have reached steady-state (Fig. 5). Ionic strengths computed from the VMINTEQ speciation model at t=21 days (see Online Resource 1 – Table S3) are slightly higher (0.0309 to 0.0324 M) than those calculated from the initial open-system modeling of CND_{MT} (0.0305 M). According to the model results: 1) the four solutions were oversaturated with respect to $Co_3O_{4(s)}$ and a suite of Mn oxides, just as they were in the solid-free, initial CND_{MT} solution, 2) the wood ash solution was oversaturated with respect to calcite, aragonite, dolomite (ordered and disordered) as well as Ni carbonate, 3) the wood ash and compost solutions were oversaturated with respect to phosphate minerals ($MnHPO_4$ and hydroxyapatite), 4) with the exception of the compost solution, all solutions were oversaturated with respect to barite ($BaSO_4$).

3.5 Chemical extractions of solid substrates and precipitates after the medium-term

sorption batch experiments

The final sequestered Ni concentrations ($q_{t(final)}$) were calculated for each reactor at t = 56 days using Eq. 1. The mean $q_{t(final)}$ values and analytical uncertainties were 742 ± 25 mg/kg for wood ash, 717 ± 25 mg/kg for compost, 622 ± 20 mg/kg for HD-peat-calcite and 610 ± 21 mg/kg for LT-peat-calcite. The lower $q_{t(final)}$ values in the peat-calcite reactors might be due to the higher solid : solution ratio within these reactors (higher *m* value in Eq. 1), caused by the addition of calcite. Ni concentrations in extraction solutions following the SPLP and SEP are presented in Table 5. The total amount of Ni extracted by SEP (i.e., sum of all fractions) were within analytical error of the calculated $q_{t(final)}$ values for all solid substrates. Results of the SEP (Fig. 6, Table 3) indicate that Ni was retained predominantly on the reducible or bound to Fe-Mn oxides fraction (F3) of the solid wood ash residue and on the oxidizable or bound to organic matter fraction (F4) in the solid compost, HD-peat-calcite and LT-peat-calcite residues. About one third of the Ni was also associated with F3 in the solid compost residue and with the carbonate bound and specifically adsorbed fraction (F2) in the solid LT-peat-calcite residue (31 %).
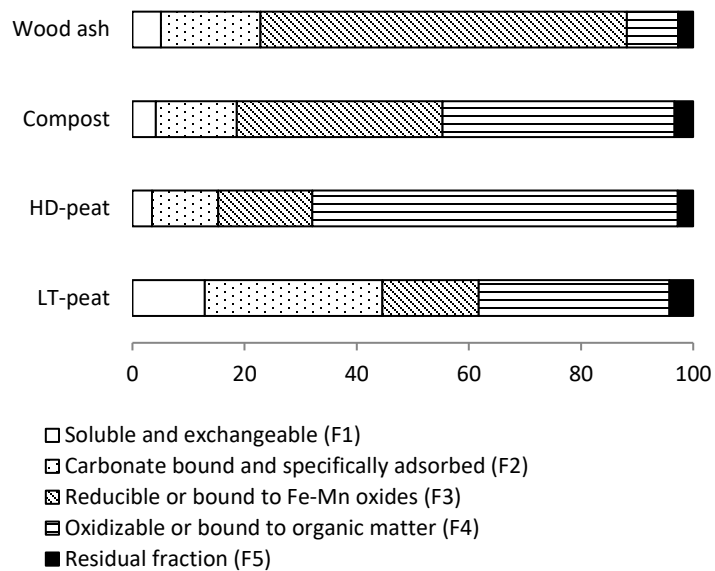
Fig. 6 Fractionation of Ni, according to the SEP applied to solid substrates and

precipitates recovered after medium-term batch sorption experiments.

Table 3. Ni concentrations in extraction solutions following SPLP and SEP of solid substrates and precipitates recovered after medium-term batch sorption experiments.

Solid substrates	Type of extraction		[Ni] in chemical extractions (mg/kg)
Wood ash	SPLP[1]		< DL
	SEP[2]	F1 [3]	36.9 ± 1.2
		F2	128 ± 4
		F3	472 ± 4
		F4	66 ± 12
		F5	19.6 ± 5.8
		Sum	722 ± 27
Compost	SPLP		3.74 ± 0.01
	SEP	F1	31.2 ± 0.3
		F2	107 ± 0.2
		F3	275 ± 32
		F4	310 ± 35
		F5	25.6 ± 2.4
		Sum	748 ± 69
HD-peat-calcite	SPLP		0.73 ± 0.07
	SEP	F1	19.1 ± 0.5
		F2	64.7 ± 0.6
		F3	91.8 ±0.4
		F4	357 ± 11
		F5	15.0 ± 1.5
		Sum	548 ± 14
LT-peat-calcite	SPLP		2.78 ± 0.11
	SEP	F1	76.9 ± 0.6
		F2	188 ± 2
		F3	103 ± 5
		F4	203 ± 15
		F5	25 ± 3
		Sum	596 ± 26

[1] SPLP results are expressed as mean ± standard deviation of [Ni] from n = 2 (duplicate samples A & B from reactor R2).[1] SEP results are expressed as mean ± standard deviation of the [Ni] from n = 2 (duplicate samples A & B from reactor R1). [3] Fraction numbers stand for: F1 - Soluble and exchangeable ; F2 - Carbonate bound and specifically adsorbed, F3 - Reducible or bound to Fe-Mn oxides, F4 - Oxidizable or bound to organic matter; F5 - Residual

4. Discussion

4.1 Effect of solution composition

In order to evaluate the effect of the CND composition on Ni sorption, final sequestered Ni concentrations ($q_{t(final)}$) from the short-term (pH7) batch experiments in this study (ionic strength of 0.03 M) were compared to those obtained from a previous experiment conducted in 0.05 M $NaNO_3$ (Table 4). Apart from the different solution compositions and slightly different ionic strengths, experimental protocols were identical between the two experiments (same substrates, apparatus, initial Ni concentrations, solid: solution ratio, volume, and reaction times). This comparison shows that the final (24 h) sorbed Ni concentrations are identical for HD-peat and compost in both types of solutions (Table 4). For algae, sawdust and wood ash, 10-20 % more Ni was sequestered from the $NaNO_3$ solution, in the presence of indifferent ions only, than from the CND solution indicating that Ni sorption might have been affected by the presence of competing cations or complex forming anions such as sulfate (Fig.1) in the CND solution. The higher q_{max} parameter of HD-peat and compost (Table 2) suggests the presence of more sorption sites and may explain why the performance of these two materials seems unaffected by the presence of competing cations.

Table 4. Comparison between final adsorbed [Ni] ($q_{t(final)}$) during short-term (24 h) experiments in $NaNO_3$ and in synthetic CND.

Experiment	Material	$q_{t(final)}$ (mg/g)	Reference
Short-term sorption experiments in 0.05M $NaNO_3$ (pH7)	Algae	0.532 ± 0.014	(Richard et al. 2020)
	Sawdust	0.508 ± 0.003	
	Wood ash	0.565 ± 0.005	
	Compost	0.706 ± 0.002	
	HD-peat	0.719 ± 0.017	
Short-term batch in 0.03M CND (pH7)	Algae	0.433 ± 0.006	This study
	Sawdust	0.427 ± 0.003	
	Wood ash	0.513 ± 0.012	
	Compost	0.705 ± 0.001	
	HD-peat	0.731 ± 0.004	

[1]Results are expressed as mean ± standard deviation using n = 2 (duplicate reactors).

4.2 Selection of the most efficient materials for medium-term batch experiments

The selection of materials for medium-term batch experiments was based on the results of short-term batch experiments using synthetic CND_{ST} and based on results of a previous study in which the material's sorption kinetics and isotherms had been evaluated during short-term adsorption and desorption experiments in 0.05 M $NaNO_3$ (Richard et al. 2020). The decision to pursue experiments with peat, compost, and wood ash was based on the following observations: 1) At pH 7, of the five substrates investigated, peat sequestered the most Ni followed by compost (see q_{max} parameter in Table 2), and these two materials also retained a higher percentage of the sorbed Ni upon exposure to a Ni-free 0.05 M $NaNO_3$ solution (Richard et al. 2020); 2) The Ni sorption kinetics were faster with peat and compost than with the other substrates (Richard et al. 2020); 3) The natural pH of compost and wood ash slurries was within the neutral range (6 to 9) (Fig. 4), meaning that these substrates could be used directly in

the field, without further pH adjustment; 4) The natural pH of the wood ash slurry (7.95) during batch experiments (Fig. 4) was higher than the pH value at which $NiCO_{3(s)}$ and calcite are oversaturated in the synthetic CND solution, implying that, in addition to surface adsorption, this material could potentially sequester more Ni by sorption/co-precipitation onto newly formed calcite; 5) Peat, compost and wood ash released less DOC upon their dispersion in water (Table 2) and would likely be more recalcitrant to degradation than algae and sawdust and thus better suited for long-term (years) field applications; 6) Although the pH of the peat slurry would have to be increased from pH ≈ 4 (Fig. 4) to pH ≈ 7, this material is readily available near many Canadian mine sites, reducing transportation costs.

4.3 Medium-term batch experiments

The four substrates tested in medium-term batch experiments performed equally well in terms of Ni removal by sequestering between 97 and 99 % of the Ni in solution (Fig. 5). These performances are compared to those observed during the short-term batch experiments under near identical solution compositions (Table 1) and, with the exception of the HD-peat-calcite, identical solid: solution ratios (Table 5). Irrespective of the experimental conditions investigated, the HD-peat and compost had similar performances whereas the performance of wood ash improved with increasing pH and equilibration time. The sorption of nickel onto solid surfaces generally increases with pH (Stumm and Morgan 1996; Zhou and Haynes 2010) as the charge of these surfaces

becomes more negative. Hence, the increased sorption capacity with higher net negative surface charge or the formation of precipitates at higher pH may have played a role in the improved performance of wood ash. Furthermore, the slightly slower sorption kinetics of wood ash in comparison to compost and HD-peat (Fig. 3) might explain the 12 % performance increase between the short-term (pH 8) and medium-term batch experiments, as both experiments were conducted at the same pH. One of the objectives of the medium-term batch experiment was to verify whether DOC release from the organic substrates would affect their Ni retention capacity. Although all substrates generally released DOC, no Ni release was observed throughout the duration (56 days) of the experiments. Some oxidation of released DOC was observed in the peat-calcite reactors in the first two weeks (as indicated by the increase in COD) without noticeable impact on soluble Ni removal from the solution.

Table 5. Percentages of Ni sequestered during short- (24 h) and medium-term (56 days) sorption experiments.

Experiment	Material	Nickel sequestered (%)
Short-term batch (pH7/pH8)	Compost	94/97
	Wood ash	69/86
	HD-peat	98/99
Medium-term batch[1]	Compost	97
	Wood ash	98
	HD-peat-calcite	99
	LT-peat-calcite	97

[1]The stabilized pH values in the medium term batch reactors were: 7.19 ± 0.14 (Compost), 8.06 ± 0.15 (wood ash) and 7.52 ± 0.11 (HD- and LT-peat-calcite).

4.4 Chemical extractions of solid substrates and precipitates after the medium-term

sorption batch experiments

The amounts of Ni leached during the SPLP (Table 3) were at least one order of magnitude lower than those released during the first step of the SEP (soluble and exchangeable fraction F1) in 0.5 M $MgCl_2$. The weak ionic strength (8.85×10^{-5} M) of the SPLP solution may explain why very little Ni was released by ion exchange to this solution in the absence of other competing ions. Results of the SEP (Table 3, Fig. 6) indicated that the proportion of Ni in the potentially mobile fraction (F1 + F2), which represents the fraction that could become an environmental risk (Agnieszka and Barbara 2012; Pinto and Al-Abed 2017; Zagury et al. 2016), was higher in the LT-peat-calcite residue (45 %) than in the other types of residues (15-23 %). Although the relatively small carbonate bound and specifically adsorbed (F2) fraction of the wood ash residue seems to imply that carbonate precipitation did not play a major role in Ni sequestration during the medium-term batch experiment, further investigations are warranted to evaluate whether carbonates are effectively dissolved during the F2 extraction with such alkaline substrates (wood ash pH is around 9). The higher Ni content of the oxidizable or bound to organic matter fraction (F4) of the HD-peat-calcite residue in comparison with the LT-peat residue is concordant with the higher total organic carbon content (53.3 %) of this substrate in comparison to LT-peat (43.5 %) (Table 2).

4.5 Sorption capacity by unit of volume

The sorption capacities of materials are typically reported on a mass basis such as mg/g.
The mass of material that may fit in a fixed or limited volume application is dictated in
part by the material's density, and therefore, for applications such as fixed-bed column
experiments or eventually field treatment systems, it is more relevant to compare the
sorption capacity of materials on a volume basis such as mg/cm^3. Sorption capacities by
unit volume of 0.50 mg/cm^3, 0.26 mg/cm^3, 0.12 mg/cm^3 and 0.02 mg/cm^3 could be
estimated for compost (density of 0.70 g/cm^3), wood ash (density of 0.35 g/cm^3), HD-
peat (density of 0.20 g/cm^3) and LT-peat (density of 0.04 g/cm^3) respectively from
medium-term batch experiments using $q_{t(final)}$ values (t = 56 days). Typically, equilibrium
experiments (sorption isotherms) are used to estimate the maximal sorption capacity of
materials. In the circum-neutral pH range, these experiments are a challenge as the
higher metal concentrations used may trigger precipitation reactions and lead to an
overestimation of the maximal sorption capacity (Richard et al., 2020). Equilibrium
experiments conducted under lower pH values may not trigger precipitation reactions,
but they could underestimate the sorption capacity as it generally increases with pH
(Fig. 4). Using the q_{max} parameter (Table 2) and previously stated substrate densities, the
estimated maximum sorption capacity by unit of volume would be 6.2 mg/cm^3 for
compost, 4.4 mg/cm^3 for HD-peat and 1.3 mg/cm^3 for wood ash. While rough
estimates, both actual (using $q_{t(final)}$) and maximum (using q_{max}) sorption capacity
values calculated reveal that compost, because of its higher density, would theoretically

sequester more Ni in a fixed-bed column experiment if sorption was the only sequestering mechanism at play.

5. Conclusions

When the pH of the synthetic CND was allowed to drift, compost, peat and wood ash sequestered the most Ni and the pH of compost and wood-ash slurries naturally remained within the circum-neutral range. The two calcite-amended peats (HD- and LT-peat), compost and wood ash performed equally well during the medium-term (56 days) experiment, sequestering over 97 % of the Ni from a 7.69 ± 0.47 mg·Ni/L CND. A sequential extraction procedure revealed that the sequestered Ni was potentially more mobile in the LT-peat-calcite-residue than in the other organic materials. For fixed volume applications such as column reactors, the density of substrates influences their sorption capacity by unit of volume, and very low density substrates such as LT-peat may be disregarded for sorption based treatment solutions. Further investigations with denser, more humified types of peats might help improve the performance of this type of substrate. Compost had the highest estimated maximal sorption capacity by unit volume, theoretically making it the most promising candidate for sorption-based fixed bed column experiments. Finally, of the three types of materials tested, wood ash was the only one to naturally increase the pH of the CND. Its performance improved as pH and exposure times were increased and further investigations are needed to assess if additional Ni could be sequestered by this substrate through precipitation mechanisms.

Acknowledgements

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