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TECHNICAL ARTICLE

Impact of Temperature and Loading on the Mitigation of AMD in Peat Biofilter Columns

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Abstract The mitigation of AMD at Canadian mine sites using passive treatment technologies requires a combined strategy that minimizes the effect of climatic variability on the treatment performance of the system. A vertical-flow combined passive treatment system was developed consisting of an oxidation/precipitation basin for excess iron removal; an unsaturated flow peat biofilter for heavy metal sorption and the reduction of oxygen concentrations; a sulfate reducing bacteria bioreactor for alkalinity generation and sulfate reduction; and, an anoxic limestone drain for alkalinity addition. Laboratory investigations were undertaken to characterize AMD mitigation through the peat biofilter under unsaturated flow conditions and to assess its performance in the combined passive system. Peat column sorption studies were conducted at 20 and 0°C to assess the effect of temperature on metal retention. At 0°C, a metal removal efficiency of $Cd < Mn < Zn < Al < Ni < Cu < Fe$ was noted. At 20°C, however, sulfate-reducing conditions developed in the column as a result of the flow regime, which facilitated the establishment of anaerobic zones within the peat column, leading to a significant increase in effluent pH and metal removal. Sequential extraction indicated that Fe, Cu, and Al were typically bound to the organic matter fraction, while Mn, Zn, Ni, and Cd were primarily associated with the exchangeable fraction.

Keywords Acid mine drainage · Adsorption · Bioremediation · Biosorption · Passive treatment · Peat biofilter · Sulfate reducing bacteria

Introduction

Over the last three decades, the mitigation of acid mine drainage (AMD) has become a significant environmental issue for the mining industry. At most active and some inactive mine sites, comprehensive systems have been developed to collect and treat acidic effluents and seepages. However, the mining industry has the potential to generate large volumes of AMD and acid generation may persist for decades after mining operations have ceased. Thus, long-term treatment may be required for effluent AMD, even under the best reclamation scenarios, to meet increasingly stringent environmental standards.

Passive treatment systems use chemical, biological and physical removal processes that interact based on ecological principles within the environment to modify AMD characteristics. These systems can be managed to control biogeochemical cycles, thereby immobilizing AMD contaminants, leading to ecological restoration through biomineralization (Kalin 2004). Combined passive strategies utilize processes that have the potential to effectively generate alkalinity, neutralize pH levels, reduce dissolved metal concentrations, and reduce sulfate concentrations (Brown et al. 2000). To date, limited information is available regarding the applicability and life expectancy of passive treatment systems at Canadian mine sites under

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Canadian climatic conditions. Canadian AMD displays strong seasonal variability in metal concentrations and flow rates. Typically, flow rates are low and metal concentrations are high in winter, while the converse is true in the spring due to spring runoff. Canadian mine sites are also characterized by harsh winters and short growing seasons. The mitigation of AMD using passive treatment technologies requires a combined strategy, which often incorporates peat as a natural biosorbent or biofilter, since it can minimize the effect of climatic variability on the treatment performance of the system.

A vertical-flow combined passive system was developed by Champagne et al. (1999, 2002, 2005). The system consisted of four components with specific treatment functions: an oxidation/precipitation basin for excess Fe removal; a peat biofilter for the biosorption of heavy metals and the establishment of anoxic conditions through aerobic biological activity; a sulfate reducing bacteria bioreactor for alkalinity generation and sulfate reduction; and an anoxic limestone drain for alkalinity addition. The performance of the peat biofilter under unsaturated flow conditions as a result of climatic variability was considered of interest due to the different biological and chemical processes taking place in saturated and unsaturated zones within the peat matrix. The main focus of this study was to investigate the effects of temperature and flow rate on metal retention and sulfate removal within the peat biofilter component of this system.

Biosorption treatment of AMD using peat relies on the removal of metal ions from solution; the primary removal mechanisms comprise ion exchange and complex formation. Peat is a complex material, consisting of cellulose, lignin and humic substances. The lignin and humic substances contain functional groups that are essential for the sorption of metal ions. The primary functional groups of lignin consist of alcohols ($R–CH_2–OH$), aldehydes (R–C=O(–H)), ketones (R–C=O(–R)), carboxylic acids (R–COOH), phenolic hydroxides (Ar–OH) and ethers ($R–CH_2–O–CH_2–R$). The key functional groups of humic substances include carboxyl (R–COOH), hydroxyl (R–OH) and carbonyl (R–C=O) groups. These functional groups can be negatively charged, which creates a strong attraction of the metal ions to the peat (Couillard 1994; Evangelou 1998; Thurman 1985). The functional groups interact with metal ions on the basis of surface adsorption, ion exchange, and complex formation, such as chelation. The adsorption reactions that occur between metal ions and peat functional groups involve water bridging of metals and the formation of either relatively weak outer-sphere complexes, or strong inner-sphere complexes. The binding of metal ions onto peat functional groups via electrostatic forces involves a relatively weak outer-sphere bond, and the metal ion can easily be exchanged by other outer-sphere complex forming ions. This interaction is also referred to as ion exchange. When a functional group, such as a hydroxyl group, becomes deprotonated, a negative charge exists at that site and metal cations are then attracted to the negative charge on the functional group and weakly bind. Inner-sphere complexation (also referred to as complex formation) and more specifically, chelation, requires two functional groups that are negatively charged and capable of forming a ring. There appears to be two modes in which this takes place. First, a metal is bound using a deprotonated hydroxyl group ($R–O^-$) and a deprotonated carboxyl group ($R–COO^-$). Second, metals may be bound by two deprotonated carboxyl groups. Metal exchange of complexed metals can occur when other cations capable of forming inner-sphere complexes are present in solution (Evangelou 1998).

In addition to ion exchange and complex formation, metal ions can also interact with peat functional groups when they become deprotonated, and the positive H^+ ion of water is attracted to the negative charge. Metal cations are then attracted to the weakly negatively charged O atom of the water molecule. This is a very weak interaction and involves metals that contain high hydration energy (Evangelou 1998).

The metal sorption capacity of peat is affected by pH; at lower pH values, sorption sites become protonated, which decreases the ability of peat to retain metals. This phenomenon creates selective sorption of cations in solution. Four important factors that determine the selectivity of cation sorption are: (1) the capacity of ions to form ion pairs; (2) the type of hydrated complex formed by the cation; (3) the types of interactions between the peat functional groups and the metal ions; and (4) the nature and abundance of functional groups within the peat (Couillard 1994).

Peat has the ability to remove a large number of dissolved metals from solution. Column tests by Ringqvist et al. (2002), using peat as a biosorbent to mitigate a synthetic sulfide mine leachate, reported removal rates up to 80, 75, 51, 70, and 77% for Cu, Cd, Fe, Ni, and Zn, respectively. Champagne et al. (2005) reported reductions of 96, 88, and 99% removal for Fe, Al, and Cu, respectively, from column experiments carried out using a synthetic AMD solution. Other metals, such as Mn Cd, Zn, and Ni were also tested, and initially, 100% retention of these metals was observed. However, these weakly sorbed metals began to break through the column after only approximately 50 days of operation. At the end of the study, metal retention of Mn, Zn, Cd, and Ni was 18, 26, 37, and 40%, respectively. Peat biofilters have been developed for the treatment of domestic and industrial wastewater. The processed *Sphagnum* peat employed in biofilters has a high capacity for contaminant adsorption, similar to the adsorptive properties demonstrated by peat in natural and constructed wetland systems. In addition, peat is a highly porous material that promotes microbial growth within its pore space and allows for the treatment of wastewaters via aerobic and anaerobic biodegradation. Peat biofilters can be designed to provide treatment throughout the entire year since they often do not freeze during the winter months as a result of sustained microbiological activity and, when designed adequately, have been reported to treat municipal and industrial wastewaters efficiently throughout the year under winter conditions (Brooks 1984).

Peat biofilters have also been employed for the mitigation of metal contaminated wastewaters, including AMD, where a number of physical, chemical, and biological processes contribute to the metal removal. Acid mine drainage abatement via biosorption can supplement other metal retention mechanisms (i.e., uptake, ion-exchange, surface adsorption, chelation, chemisorption, complexation, and precipitation). Smith and Kalin (1989) evaluated the self-sustaining and maintenance-free Chara process for treating drainage water from a uranium mine in Northern Saskatchewan. Laboratory experiments by Vatcharapijarn et al. (1994), using microbial mats immobilized on glass wool, evaluated the removal of Zn and Mn from contaminated waters; they found that extracellular metal deposits could minimize toxic effects in the biological system. Researchers have also researched the genetic engineering of microorganisms to sequester metals such as Au, Ag, Pt, Cd, Co, Cu, U, and Hg, mainly for the purpose of metal extraction and recovery (Ledin and Pedersen 1996; Smith et al. 1994). The use of non-living biomass for reducing metal concentrations in mine drainage has also been investigated. The metal sorption capacities of natural carbonaceous materials, including wood, bark, cork, peat, modified peat-resin, oyster shells, peanut shells, cocoa shells, corn cobs, vermiculite, perlite, fusinite, lignite, bituminous coal, activated chars, anthracite, and non-viable activated sludge have been reported (Allen et al. 1997; Blais et al. 2003; Hanzlik et al. 2004; Sun et al. 2004; Utgikar et al. 2000). Removal mechanisms depend on the nature and origin of the material utilized (Ringqvist and Oborn 2002; Ringqvist et al. 2002; Twardowska et al. 1999), the degree of pre-treatment applied to the material, and the composition of the metal solution requiring treatment (Brown et al. 2000). Other operational factors, such as the presence of complexing anions, contact mode (Twardowska and Kyziol 2003), and pH (Aldrich and Feng 2000; Ma and Tobin 2004) are also important. Research by Arnfalk et al. (1996) investigating peat, various soil materials, and minerals indicated that the organic content of soils was the most significant parameter affecting metal sorption, followed by surface area, particle size, and extractable metal content.

The use of commercial non-living biomass to reduce dissolved metal concentrations from mine waste environments has also been described. One biosorbent material used to treat AMD is BIO-FIX (Biomass-foam immobilized extractant), where beads are fabricated from dried non-living biomass such as marine algae (*Ulva* sp.), blue-green algae (*Spirulina* sp.), yeast (*Saccharomyces cerevisiae*), common duckweed (*Lemna* sp.), and finely ground *Sphagnum* peat moss, blended into a high-density polysulfone dissolved in an organic solvent. Bennett et al. (1991) and Jeffers et al. (1989) recommended using BIO-FIX to adsorb contaminants from dilute AMD streams containing metal concentrations below 15 mg/L. The bio-recovery system AlgaSORB 2, a preparation of immobilized algae (mainly *Chlorella vulgaris*), was proposed by Darnall et al. (1989) and was found to effectively recover metals such as Cu, Hg, or Cd from contaminated ground water. Médiaflex$_{MC}$, a biofilter material composed of *Sphagnum* peat moss and carbon material, has adsorptive and chemical precipitation properties (Bélanger et al. 1995).

Experimental

The effect of flow rate and AMD constituent concentration on heavy metal adsorption and sulfate reduction in a peat biofilter was tested at temperatures of 0 and 20°C in column experiments. The metal composition of the peat (on a mass basis) prior to the application of AMD is provided in Table 1. Following each column experiment, a sequential extraction procedure was performed to determine the

Table 1 Total metal ion concentrations in initial peat material on a mass basis

Element	Total ion concentration (μg/g)
Ca	7,420
P	440
K	4,180
Mg	4,070
Fe	3,790
Mn	16.6
Mo	88.0
As	93.6
Cd	0.8
Co	24.1
Cr	15.8
Cu	301
Ni	7.9
Pb	13.3
Se	5.7
Zn	53.2

associative preference of each metal for the peat biofilter material under different AMD constituent concentrations, flow rate conditions and temperature regimes.

Column Experimental Set-up

Prior to packing, milled New Brunswick peat was hand-sieved with a 0.6 cm (¼ in.) sieve. The fraction of peat retained on the sieve was collected and allowed to air-dry over a 24 h period. Eight stainless steel columns (14.6 cm inside diameter), each insulated with two layers of standard pipe insulation, were packed with peat in 10 cm lifts to a depth of 45 cm. The columns were packed at an average dry density of approximately 194 kg/m^3, corresponding to a saturated hydraulic conductivity of 1.02×10^{-4} m/s, a porosity of 77.4%, and a water retention capacity of 364%.

To determine the effect of constituent concentration, two of the columns were supplied synthetic AMD with the high constituent concentration composition presented in Table 2, while the other two columns were fed a 25% volume to volume (V/V) dilution of the synthetic AMD mixture with distilled water, to provide the low constituent concentration composition outlined in Table 2. The flow rate was 1.37 L/day (82 L/m^2 per day) for two of the columns, while the other two columns each received 0.685 L/day (41 L/m^2 per day). These flow rates resulted in unsaturated flow conditions, with aerobic and anaerobic zones within the peat columns. An unsaturated flow regime represents field conditions. Four experimental conditions were tested by combining the AMD constituent concentrations and flow rates at 0 and 20°C: (1) high-flow, high AMD strength (HQ-HC); (2) high-flow, low AMD strength (HQ-LC); (3) low-flow, high AMD strength (LQ-HC); and (4) low-flow, low AMD strength (LQ-LC).

Operational Conditions

The experiments ran continuously for a period of 75 days, one at an ambient laboratory temperature of 20°C and the other at an ambient temperature of 0°C in a cold room located in the Geocryology Laboratory at Carleton University. After the 75 day sorption period, all columns were flushed with a

Table 2 Average synthetic AMD influent concentrations for column experiments at 0 and 20°C

	High constituent concentration				Low constituent concentration			
	Sorption		Desorption		Sorption		Desorption	
	Mean (mg/L)	St. dev. (mg/L)	Mean (mg/L)	St. dev. (mg/L)	Mean (mg/L)	St. dev. (mg/L)	Mean (mg/L)	St. dev. (mg/L)
0°C								
pH	3.0	0.14	3.9	0.16	3.4	0.28	4.0	0.23
DO	6.9	0.60	6.9	0.14	6.8	0.63	6.2	0.56
SO_4	3,150	104	183	12.7	776	46.3	194	9.19
Fe(II)	197	9.02	10.9	0.95	51.3	2.72	10.4	0.77
Al(III)	90.9	4.63	4.8	0.0	21.4	2.46	4.8	0.0
Zn(II)	107	8.05	5.2	0.41	20.8	3.57	5.0	0.45
Mn(II)	24.9	1.21	1.2	0.13	6.1	0.81	1.4	0.21
Ni(II)	17.7	3.40	1.3	0.04	4.4	0.80	1.3	0.63
Cu(II)	18.3	1.89	1.1	0.03	4.9	0.38	1.1	0.03
Cd(II)	6.0	0.35	0.5	0.06	1.5	0.33	0.5	0.13
20°C								
pH	3.1	0.29	3.7	0.04	3.6	0.32	3.8	0.14
DO	5.9	0.36	6.3	0.13	5.9	0.57	6.0	0.71
SO_4	2,999	36.9	170	–	803	54.3	145	–
Fe(II)	191	10.6	9.9	1.28	51.0	3.6	9.9	0.43
Al(III)	87.6	2.38	4.4	0.36	23.4	1.54	4.3	0.27
Zn(II)	93.1	13.7	5.0	0.60	21.5	2.70	5.2	0.30
Mn(II)	25.2	1.11	1.4	0.21	6.7	0.47	1.4	0.05
Ni(II)	20.3	1.24	1.1	0.22	4.9	0.52	1.1	0.28
Cu(II)	18.4	0.59	1.0	0.07	5.0	0.32	0.6	0.46
Cd(II)	6.10	0.53	0.3	0.08	1.7	0.13	0.4	0.20

Synthetic AMD chemical constituents: $FeSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $Al_2(SO_4)_3{\cdot}16H_2O$, $MnSO_4{\cdot}H_2O$, $NiSO_4{\cdot}6H_2O$, $CuSO_4$, $3CdSO_4{\cdot}8H_2O$, K_2SO_4, Na_2SO_4

5% V/V mixture of the high-strength synthetic AMD in distilled water at twice the flow rate, providing the desorption composition noted in Table 2, for a period of 10 days. The average pH of the synthetic solution was increased to 3.9 during the desorption phase of the experiment. This was performed to quantify the level of desorption that might be expected in the field during the spring high flow when constituent concentrations would be low.

Sampling Procedure and Analysis

Three times per week, a 20 mL effluent sample from each column was collected to measure dissolved oxygen (DO), metal concentrations and pH. Dissolved oxygen concentrations were measured using a WWR DO meter (model 34105–004). The pH of the samples was determined using a WWR pH/mV/temperature meter (model 34105–002). The samples were then filtered through a 0.45 µm Millipore filter and preserved with concentrated HCl to maintain a solution pH of 2. Samples were analyzed for metal concentrations using ICP-AES analysis at Carleton University. Fifteen mL samples were collected using a 20 mL syringe once per week for sulfate concentration analysis at Caduceon Laboratories. Sulfate removal rates were computed from the flow rate (Q, m^3/day), the volume of peat in the column (V, m^3), the mean influent concentration [$(SO_4^{2-})_o$, mg/L], and the measured effluent concentrations [$(SO_4^{2-})_e$, mg/L], as shown in Eq. 1.

$$\frac{\Delta\left[SO_4^{2-}\right]}{\text{day}} = \frac{Q\left(\left[SO_4^{2-}\right]_o - \left[SO_4^{2-}\right]_e\right)}{V}. \tag{1}$$

Sequential Extraction Procedure and Analysis

Once the adsorption/desorption experiment was completed, the peat from each of the columns was dissected into five 9.2 cm layers from the top (1) to bottom (5) of the column. The layered sections of peat were then oven-dried at 104°C for a period of 48 h. After drying, each layer was mixed thoroughly to obtain a more uniform material. A relative measure of the adsorption of metals onto the various fractions of the contaminated peat was assessed through a sequential extraction procedure modified from Tessier et al. (1979) and Wasay et al. (1998) for use with peat materials. Heavy metals were assessed with respect to the following operationally defined fractions of the peat material: (1) water extractable fraction (W); (2) exchangeable fraction (Ex); (3) Fe–Mn oxide bound fraction (Ox); (4) organic matter bound fraction (OM); and (5) residual metal fraction (RM). Metal concentrations were determined by ICP-AES analysis.

Water Extractable Fraction (W): This procedure is employed to release metals weakly bound to the peat to the water extractable fraction. For each of the dried peat layers, 5 samples weighing approximately 10 g were collected. These samples were then mixed to form a representative composite sample. About 100 mL of distilled water was added to 5 g of the blended samples and the mixtures were placed on a reciprocating shaker for a period of 2 h at 150 rpm at room temperature. The solutions were filtered with a 0.45 µm Millipore filter, the supernatant was collected and preserved with HCl to maintain a sample pH of 2. The solid fraction and filter were retained for subsequent exchangeable fraction analysis.

Exchangeable Fraction (Ex): Metal ions physically bound to the peat by electrostatic attraction to negatively charged sites via cation exchange are released in the exchangeable fraction procedure. The filters and solids retained from the water extractable procedure were mixed with 100 mL of 0.1 M $CaCl_2$ and returned to the reciprocating shaker for 2 h at 150 rpm under room temperature conditions. The solutions were filtered with a 0.45 µm Millipore filter, the supernatant was collected and preserved with HCl to maintain a sample pH of 2. The solid fraction and filter were retained for subsequent Fe–Mn oxide-bound fraction analysis.

Oxide-Bound Fraction (Ox): This procedure releases metal ions attached to amorphous or poorly crystallized Fe–Mn oxides or equivalent materials. The filters and solids retained from the exchangeable fraction procedure were mixed with 100 mL of 0.05 M hydroxylamine hydrochloride (NH_2OHHCl). The samples were shaken at 150 rpm for 12 h under room temperature conditions. The solutions were filtered with a 0.45 µm Millipore filter, and the supernatant was collected and preserved with HCl to maintain a sample pH of 2. The solids and filter were retained for subsequent organic matter-bound fraction analysis.

Organic Matter-Bound Fraction (OM): In this procedure, metals bound to the organic matter are released via oxidation with 30% hydrogen peroxide (H_2O_2). The filters and solids retained from the Fe–Mn oxide bound fraction procedure were mixed with 10 mL of distilled water and 10 mL of 30% H_2O_2 buffered to a pH of 2 with 0.02 M HNO_3 The samples were digested for 60 min at room temperature with occasional manual agitation. The solution was then digested at 85°C until the volume was reduced to 3 mL. Another 10 mL of 30% H_2O_2 buffered to a pH of 2 with 0.02 M HNO_3 was slowly added and digested at 85°C until the organic matter turned to ash and 10–15 mL remained. Next, the solution was allowed to cool and 50 mL of 1 M ammonium acetate (NH_4Ac) was added and shaken for 12 h at 150 rpm at room temperature. This reagent was employed to unbind any solid metals adhering to the bottle and place them in the liquid phase. The solutions were filtered with a 0.45 µm Millipore filter and the supernatant was collected and preserved with HCl to maintain a sample pH of 2. The solids and filter were retained for subsequent residual metal fraction analysis.

Residual Metal Fraction (RM): The heavy metals that were not released in the previous fractions were unbound by digesting the filters and solids retained from the organic matter-bound fraction with 30 mL of aqua regia solution (3:1 HCL:HNO_3 mixture) at 100–130°C until the solution was clear, which varied from hours to days depending on sample composition. The solutions were then filtered with a 0.45 µm Millipore filter and the supernatant was collected and preserved with HCl to maintain a sample pH of 2.

Results

Metal Constituents

Metal concentrations were monitored throughout the 85 day sorption/desorption column experiment. Cumulative metal retentions for the different loading conditions at 0 and 20°C are presented in Figs. 1 and 2, respectively. For this experiment, breakthrough was defined as the point where the cumulative metal mass retained was less than 90% of the cumulative metal mass added to the system at a given time, and was computed according to Eq. 2.

$$\text{Cumulative metal retention } (\%) = \left[1 - \left(\frac{\sum Q_e C_e}{\sum Q_i C_i}\right)\right](100\%) \qquad (2)$$

where Q_e is the effluent flow rate (L/day), C_e is the effluent constituent concentration (mmol/L), Q_i is the influent flow rate (L/day), and C_i is the influent constituent concentration (mmol/L). This breakthrough definition was employed to facilitate a comparison between the columns under different loading conditions and temperature and to readily identify trends while minimizing the effects of effluent concentration variability anticipated in these types of systems using natural biosorbents such as peat. Table 3 summarizes the cumulative metal loading (mmol) and corresponding volumetric throughput (L) noted for individual metals in each of the columns at the time breakthrough was reached under the various column loading and temperature conditions. In columns where breakthrough was not observed, a percent retention was computed from the ratio of cumulative mass retained to total cumulative mass added, and averaged from days 12 to 75.

The retention of Fe was generally found to be greater than 96% in the columns where breakthrough was not observed under loading conditions at 0 and 20°C. Breakthrough was noted in the LQ-LC and HQ-LC columns at 20°C (Fig. 2b, d). In both cases, however, removal efficiencies after the 10% cumulative breakthrough were found to improve with time. Cu retention was also found to be higher than 96%

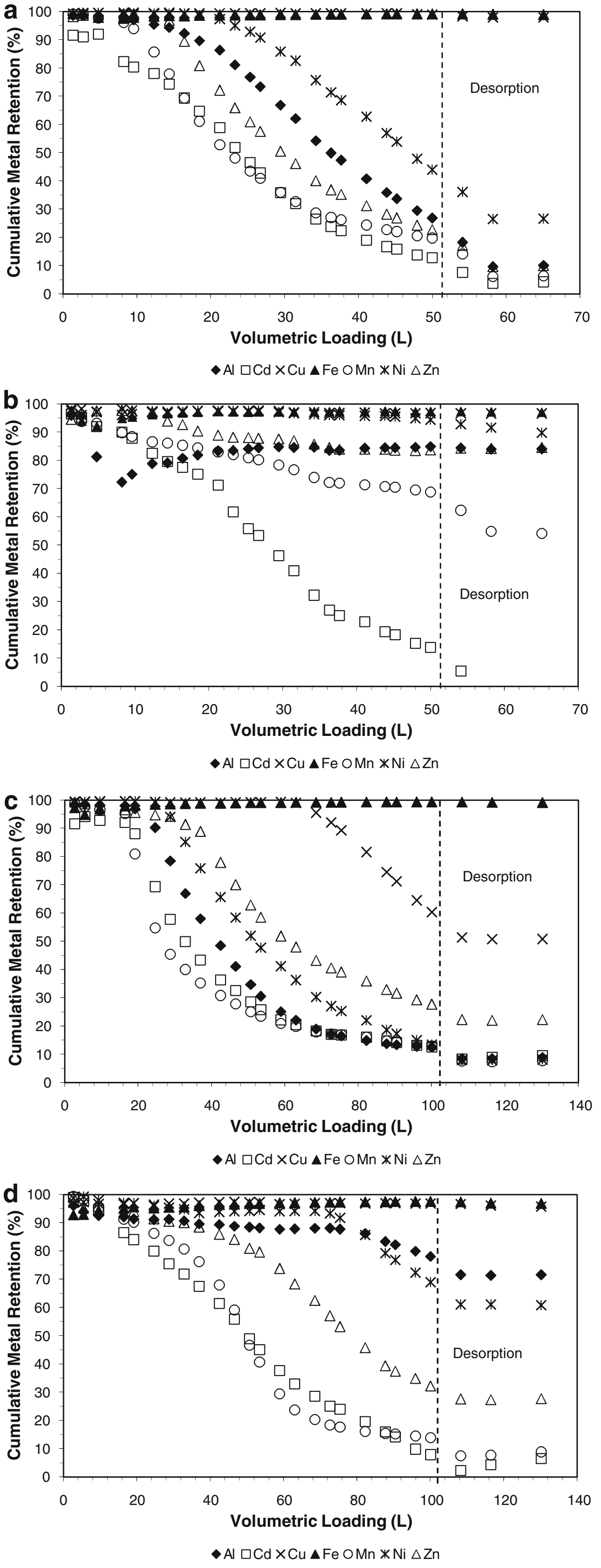

Fig. 1 Metal breakthrough with volumetric throughput for **a** LQ-HC, **b** LQ-LC, **c** HQ-HC, and **d** HQ-LC conditions at 0°C

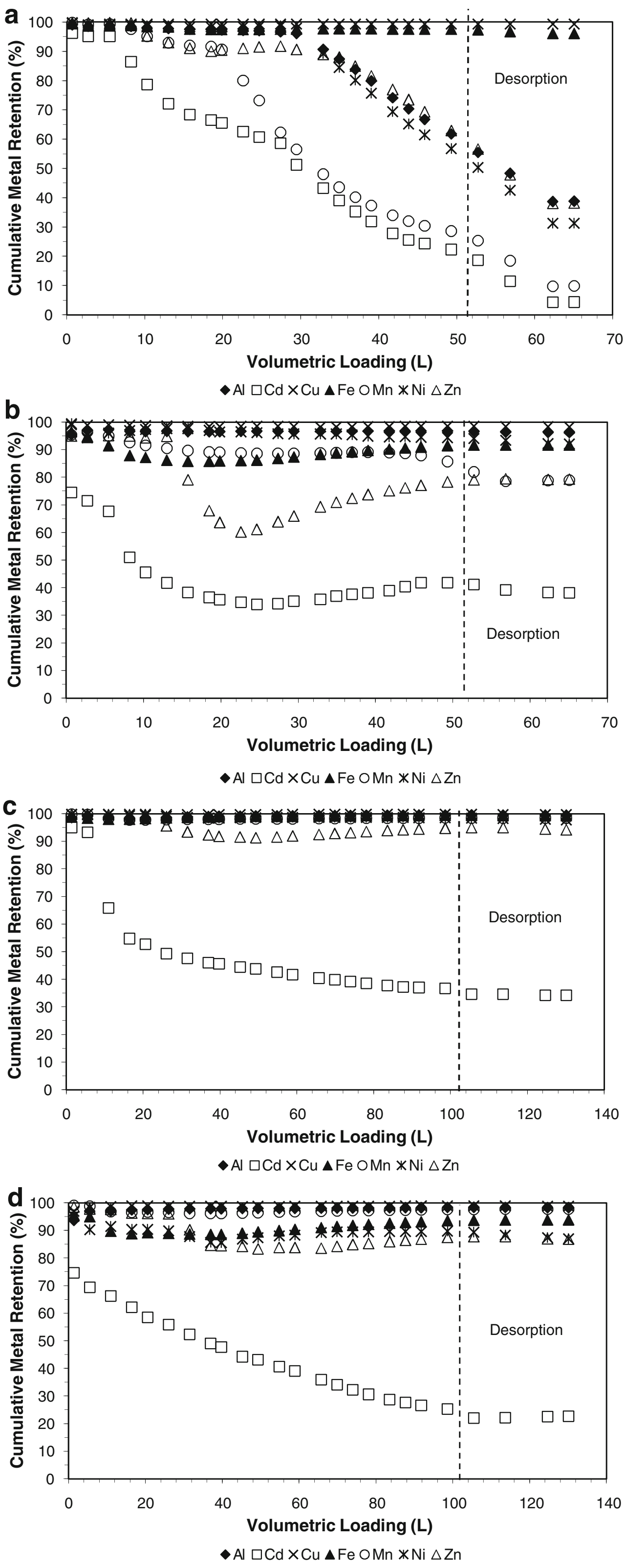

Fig. 2 Metal breakthrough with volumetric throughput for **a** LQ-HC, **b** LQ-LC, **c** HQ-HC, and **d** HQ-LC conditions at 20°C

under each of the loading conditions at 0 and 20°C. Breakthrough was only observed in the HQ-HC column at 0°C (Fig. 1c), after 55 days (75.2 L) and a cumulative Cu loading of 21.1 mmol (Table 3). At 0°C, Cu desorption was observed in the LQ-HC, HQ-HC and HQ-LC columns (Fig. 1a, c, d), while no desorption was apparent at 20°C. Under cold temperature conditions, Al breakthrough was noted in all of the columns at cumulative loadings of LQ-LC (3.3 mmol) < HQ-LC (28.2 mmol) < LQ-HC (63.7 mmol) < HQ-HC (85.6 mmol) (Table 3). The removal of Al was generally found to be higher than 96% at 20°C (Fig. 2b–d). The retention of Cd and Mn in the columns was relatively poor under all loading and temperature conditions (Figs. 1, 2). At 0°C, Cd breakthrough occurred at loadings of LQ-LC (0.08 mmol) < HQ-LC (0.1 mmol) < LQ-HC (0.5 mmol) < HQ-HC (0.9 mmol), while in the columns at 20°C, Cd breakthrough from the columns was noted at loadings of LQ-LC (0.01 mmol) ≈ HQ-LC (0.01 mmol) < LQ-HC (0.4 mmol) ≈ HQ-HC (0.4 mmol). Manganese breakthrough was observed in all of the columns at 0°C, as well as in the LQ-HC and LQ-LC columns at 20°C (Fig. 2a, b). In columns at room temperature, breakthrough was noted after a Mn loading of 1.7 mmol and 8.9 mmol for the LQ-LC and LQ-HC columns, respectively (Table 3). For the cold temperature columns, breakthrough from the columns was found to occur at loadings of LQ-LC (0.8 mmol) < HQ-LC (2.0 mmol) < LQ-HC (5.1 mmol) < HQ-HC (7.9 mmol). Zn and Ni exhibited similar responses. Zn breakthrough from the columns at 0°C (Table 3) was noted as LQ-LC (5.6 mmol) < HQ-LC (10.3 mmol) < LQ-HC (28.7 mmol) < HQ-HC (61.1 mmol). In the columns at 20°C, cumulative Zn loadings of 3.6 mmol, 9.9 mmol and 42.6 mmol were determined for the LQ-LC, HQ-LC, and LQ-HC columns, respectively. Recoveries in Zn removal efficiencies were observed in the LQ-LC, HQ-LC, and HQ-HC columns throughout the course of the experiment at 20°C (Fig. 2b, c, d). Ni breakthrough from the columns occurred as follows (Table 3) at 0°C: LQ-LC (4.1 mmol) < HQ-LC (5.7 mmol) < LQ-HC (7.4 mmol) < HQ-HC (7.5 mmol). At 20°C, Ni breakthrough was only noted for the HQ-LC (1.9 mmol) < LQ-HC (11.0 mmol) columns (Fig. 2a, d). In the columns where breakthrough was not observed, Ni retention was relatively high with 95.9% (SD 1.08) and 98.6% (SD 0.28) noted under the LQ-LC and HQ-HC loading conditions (Fig. 2b, c).

Other Constituents

Effluent pH values and sulfate removal rates are plotted in Figs. 3 and 4, respectively. Effluent pH values were relatively constant at 0°C (Fig. 3a), with mean values of 3.0,

Table 3 Cumulative constituent loading and volumetric throughput observed at the breakthrough of individual metals in peat filter columns under different temperature and loading conditions

	Metal	LQ-HC		LQ-LC		HQ-HC		HQ-LC	
		Metal loading (mmol)	Volumetric throughput (L)	Metal loading (mmol)	Volumetric throughput (L)	Metal loading (mmol)	Volumetric throughput (L)	Metal loading (mmol)	Volumetric throughput (L)
0°C	Fe	NBT	NBT	NBT	NBT	NBT	NBT	NBT	NBT
	Al	63.7	18.1	3.3	3.4	85.6	24.7	28.2	35.6
	Zn	28.7	16.1	5.6	18.9	61.1	35.6	10.3	33.1
	Mn	5.1	11.0	0.8	8.2	7.9	17.1	2.0	19.4
	Ni	7.4	27.4	4.1	64.6	7.5	30.8	5.7	78.0
	Cu	NBT	NBT	NBT	NBT	21.1	75.2	NBT	NBT
	Cd	0.4	5.5	0.08	8.1	0.9	17.8	0.1	13.6
20°C	Fe	NBT	NBT	5.9[a]	6.8	NBT	NBT	9.5*	10.8
	Al	109	34.3	NBT	NBT	NBT	NBT	NBT	NBT
	Zn	42.6	33.9	3.6	14.4	NBT	NBT	9.9*	31.7
	Mn	8.9	20.2	1.7	13.9	NBT	NBT	NBT	NBT
	Ni	11.0	32.6	NBT	NBT	NBT	NBT	1.9*	25.9
	Cu	NBT	NBT	NBT	NBT	NBT	NBT	NBT	NBT
	Cd	0.4	7.2	0.01	0.3	0.4	5.6	0.01	0.3

NBT no breakthrough

[a] Reached 10% breakthrough and then retention increased

3.3, 2.9, and 3.3 measured, from day 12 to 75, in the LQ-HC, LQ-LC, HQ-HC, and HQ-LC columns, respectively. At 20°C, low-flow effluent pH values were also constant (Fig. 3b). From days 12 to 75, the LQ-HC and LQ-LC columns recorded mean values of 3.2 and 3.5. Under high-flow conditions, however, the effluent pH began to increase significantly after 19 days (26.0 L) for the HQ-HC column; the same thing occurred after 43 days (58.9 L) for the low influent concentration column. The pH rises coincided with an increased odor emanating from each column, indicating the establishment of anaerobic activity, likely the presence of sulfate reducing bacteria, in these columns. The highest sulfate removal rates were observed in the high-flow columns at 20°C (Fig. 4b). In the columns operating at 0°C (Fig. 4a), sulfate removal rates appeared to be high initially, but were found to gradually decrease with time. Measured effluent DO concentrations were markedly lower in the columns at 20°C than those at 0°C. At 0°C, mean effluent DO concentrations greater than 5.5 mg/L were noted in each of the columns. Under warm temperature conditions, however, all effluent DO concentrations were less than 2 mg/L.

Sequential Extraction

The aim of the sequential extraction procedure was to determine the relative distribution of metals throughout the column depth, as well as the dominant fractions to which metals were bound with depth within the peat filter after 75 days of continuous AMD application under the different loading and temperature conditions.

Low-Flow High AMD Concentration: The distribution of metals within the LQ-HC columns at 0 and 20°C is illustrated in Fig. 5. Under these experimental conditions, Al, Zn, Mn, Ni, and Cd were found to be well distributed throughout the depth of the column. The breakthrough of these metals was noted in the LQ-HC columns at both temperatures (Figs. 1a, 2a), which would be consistent with an even distribution throughout the peat depth. Breakthrough of Fe and Cu was not observed in either of the LQ-HC columns (Figs. 1a, 2a), which can be explained in terms of their binding fraction. Figure 5c and d demonstrate the percentage of total metal mass retained per fraction bound at 0 and 20°C. In each of the columns, Zn, Mn, Ni, and Cd were associated with the exchangeable fraction, while Cu and Fe were bound to the organic matter fraction. Aluminum was generally bound to the organic matter and residual fractions under these loading conditions. The association with the residual fraction was probably due to Al hydroxide precipitation within the column and/or the initial Al composition of the peat (Table 1). The relatively constant distribution of Al ions in association with this fraction throughout the depth of the column would suggest the latter. Aluminum precipitation would have resulted in a

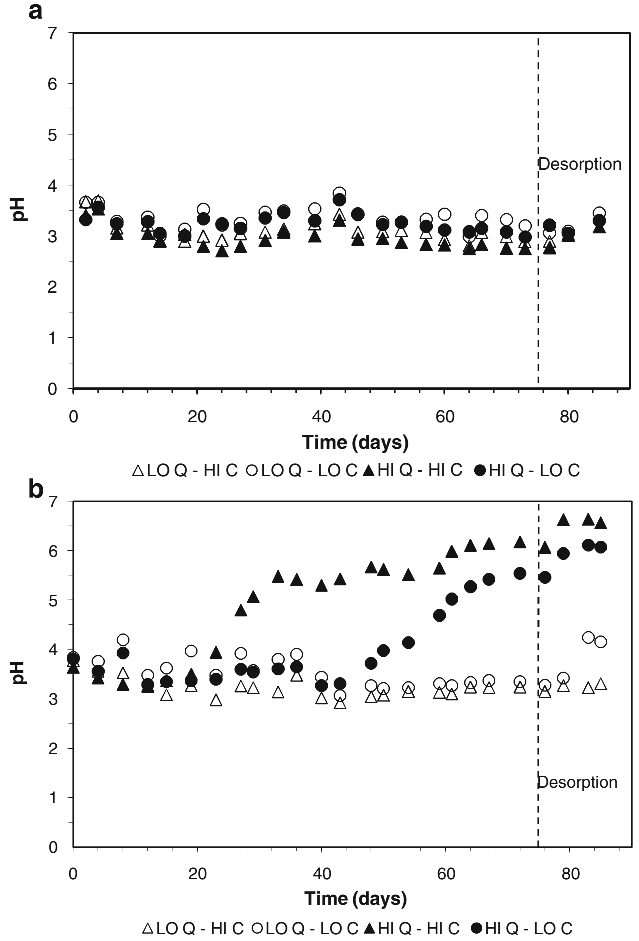

Fig. 3 Peat column effluent pH for LQ-HC, LQ-LC, HQ-HC and HQ-LC loading conditions at **a** 0°C and **b** 20°C

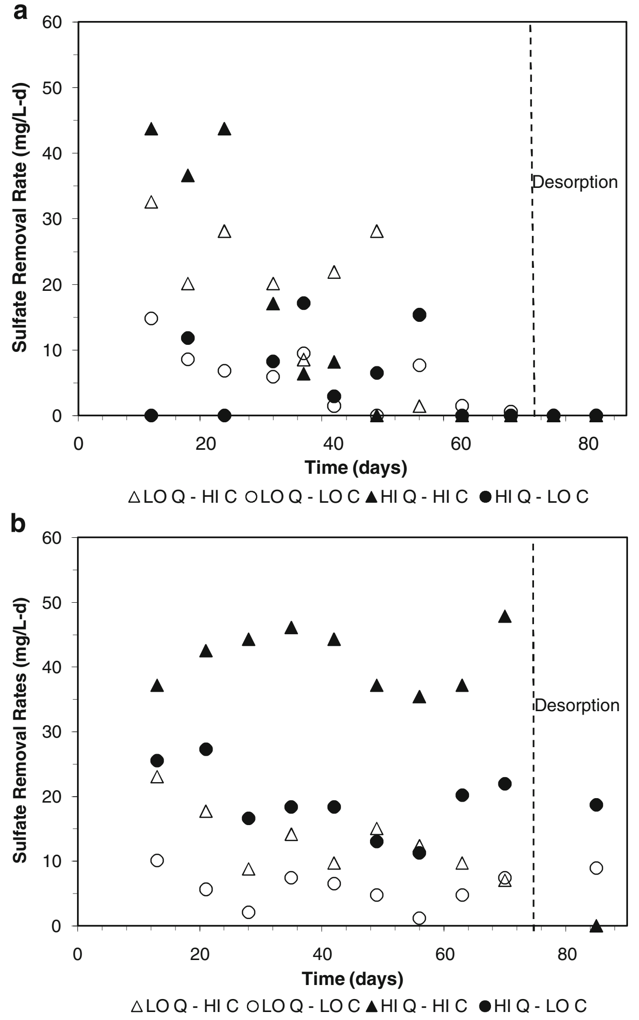

Fig. 4 Peat column sulfate removal rates for LQ-HC, LQ-LC, HQ-HC and HQ-LC loading conditions at **a** 0°C and **b** 20°C

comparatively higher retention in the upper layers of the column due to the filtering affect of the peat material, as well as increased Al removal efficiencies, neither of which was observed. The flushing of the columns with dilute AMD generally had a lower impact on Cu and Fe (Figs. 1a, 2a), which were largely bound to the organic matter fraction (Fig. 5c, d), while a decrease in cumulative metal retention was noted for Zn, Mn, Ni, and Cd, which were primarily associated with the exchangeable fraction.

Low-Flow Low AMD Concentration: The responses of the columns to the LQ-LC loading at 0 and 20°C were similar to the response observed in the LQ-HC. The distribution of metals with depth is presented in Figs. 6a, b for the 0 and 20°C cases, respectively. Aluminum, Zn, Mn, and Cd were found to be evenly distributed through the depth of the LQ-LC columns at both temperatures, consistent with the observed breakthrough of these metals under these experimental conditions (Figs. 1b, 2b). The breakthrough of Cu was not observed in either of the LQ-LC columns. Cu and Fe were strongly associated with the first layer of the peat column; however, there was a slightly higher distribution of Fe in the lower layers as well (≈10%), which was probably due to the initial composition of the peat material (Table 1) rather than the removal of Fe. The higher retention of Fe and Cu observed in the columns was probably due to their association with the organic matter fraction. Figure 6c and d demonstrate the percentage of metal mass retained per fraction bound at 0 and 20°C. At 0 and 20°C, Zn, Mn, Ni, and Cd were largely bound to the exchangeable fraction, while Cu and Fe were primarily associated with the organic matter fraction. Once again, it is plausible that a weaker association of Zn, Mn, Ni, and Cd for the exchangeable fraction might have resulted in the preferential displacement of these metals by Fe, Cu, or Al. The gradual recovery of the cumulative metal retention curves noted for Fe, Mn, and Zn, and absence of Ni breakthrough at 20°C (Fig. 2b) might suggest the establishment of sulfate reducing conditions and the start of biologically mediated metal sulfide precipitation. However,

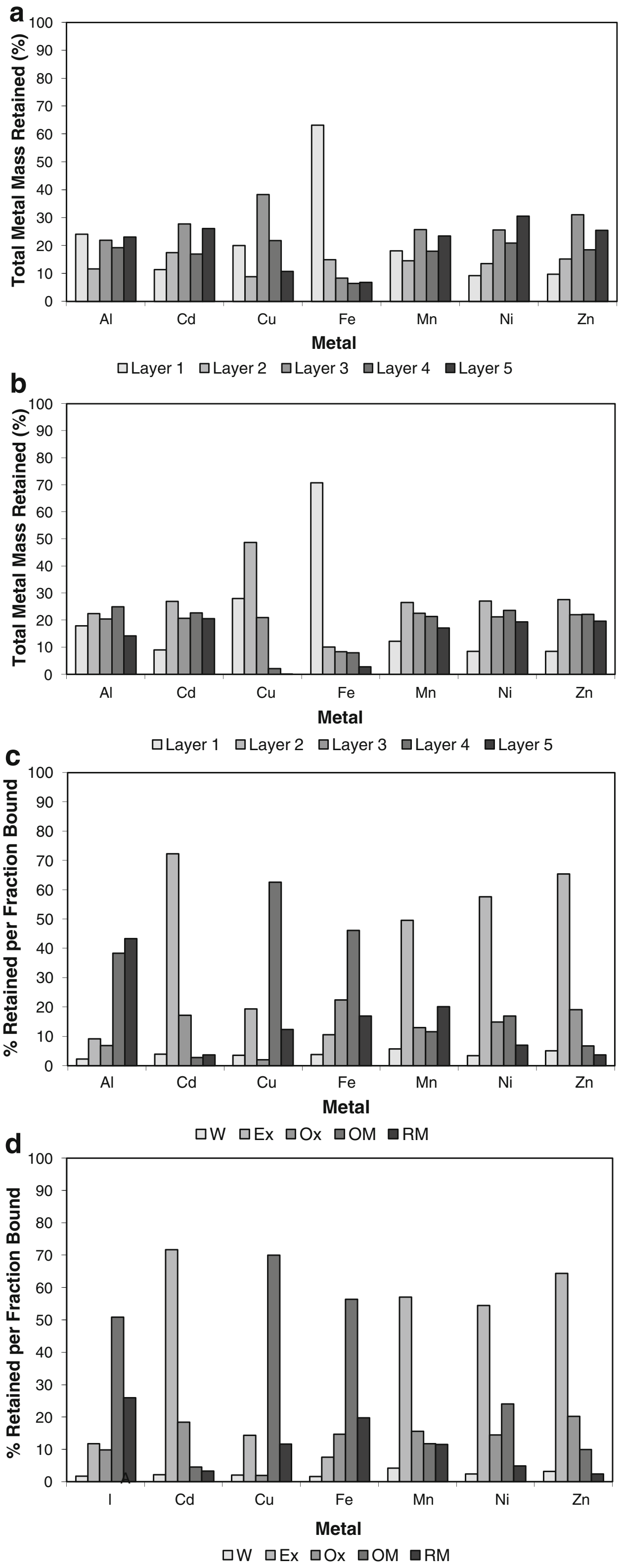

Fig. 5 Metal mass retention in LQ-HC column: per layer at **a** 0°C and **b** 20°C, and per fraction bound at **c** 0°C and **d** 20°C

this trend could not be confirmed with the effluent pH (Fig. 3b) and sulfate (Fig. 4b) data. Flushing of the columns with dilute AMD did not significantly affect Cu, Fe, Al, or Zn metal retention at either temperature regime (Figs. 1b, 2b). The desorption of Mn, Ni, and Cd was noted at 0°C, but the effect was dampened at 20°C, which may have been due to the contribution of metal removal mechanisms other than sorption, such as metal sulfide precipitation (Fig. 6c, d).

High-Flow High AMD Concentration: The HQ-HC column responses to the loadings at 0 and 20°C are illustrated in Fig. 7. Under these experimental conditions, the breakthrough of all metals with the exception of Fe was observed at 0°C (Fig. 1c), while Cd breakthrough alone occurred at 20°C (Fig. 2c). At 0°C, the metals were generally found to be well distributed throughout the depth of the HQ-HC column (Fig. 7a), which is consistent with the observed metal breakthroughs. The response of the HQ-HC column at 20°C was much different, where Fe, Al, and Cu were largely retained within the top layers, while Zn, Mn, Ni, and Cd retention was associated with the mid-layers, with very little retention occurring in the final layer (Fig. 7b). This response is consistent with the comparatively low breakthrough noted in the column (Fig. 2c). Figure 7c and d demonstrate the percentage of metal mass retained per fraction bound at 0 and 20°C. At 0°C (Fig. 7c), metal retention was in reasonable agreement with that described in the two previous cases, where Fe and Cu were primarily associated with the organic matter fraction; Zn, Mn, Ni, and Cd were mostly retained by the exchangeable fraction; and Al demonstrated a strong association with the residual fraction as well as the organic matter fraction. The higher retention of metals at 20°C, on the other hand, was found to coincide with a deviation from the preferred binding fractions reported in the two previous cases and at 0°C under the HQ-HC conditions. In the second to fourth layers of the peat column, Fe and Cu, as well as Zn, Mn, and Ni were mostly bound to the organic matter and residual fractions (Fig. 7d). This could be indicative of the establishment of biological growth and the sorption of these metals onto the growing biofilm, or removal due to metal sulfide precipitation where zones of anaerobic sulphate reducing conditions were established within the column. The development of anaerobic conditions and the establishment of a sulfate reducing environment is supported by the low effluent DO concentrations and higher sulfate (Fig. 4b) utilization rates, as well as the significant increase in pH (Fig. 3b) under the HQ-HC loading conditions at 20°C. The flushing of the columns with dilute AMD had a much lower impact at 20°C than at 0°C (Figs. 1c, 2c). At 0°C, a decrease in cumulative metal

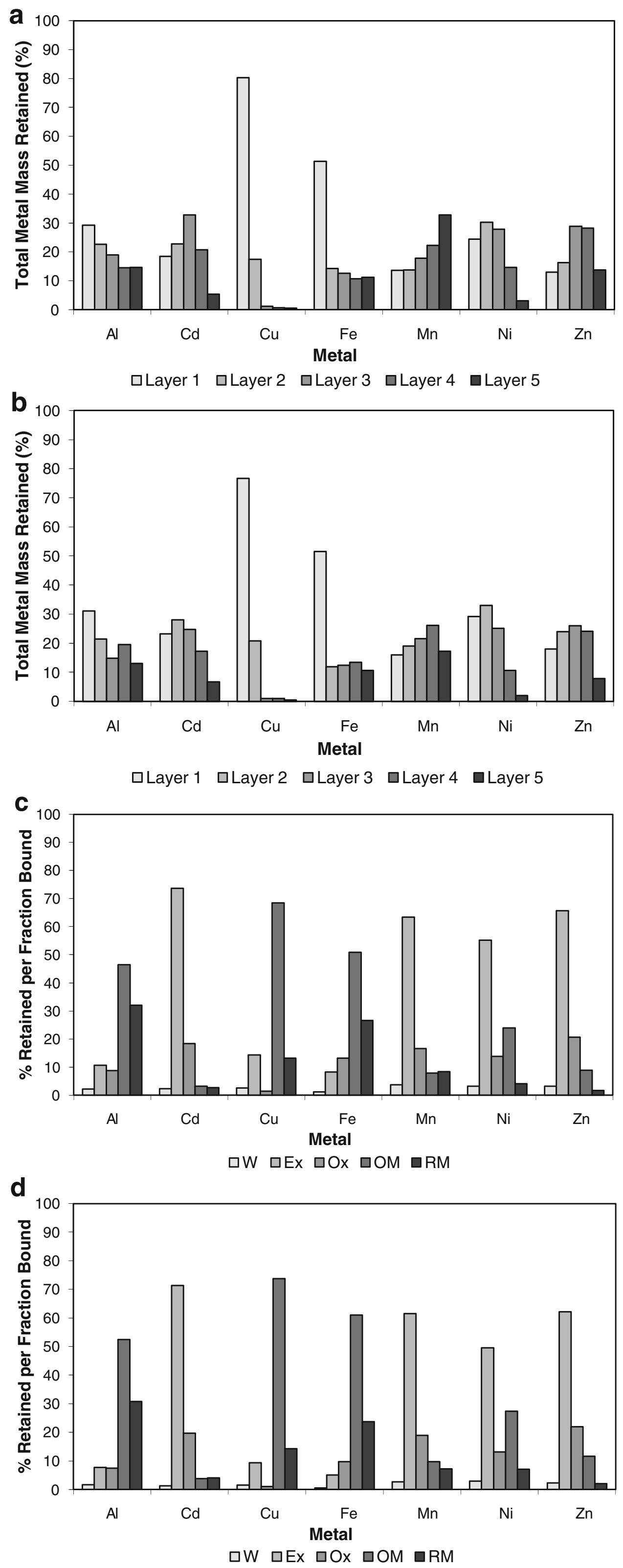

Fig. 6 Metal mass retention in LQ-LC column: per layer at **a** 0°C and **b** 20°C, and per fraction bound at **c** 0°C and **d** 20°C

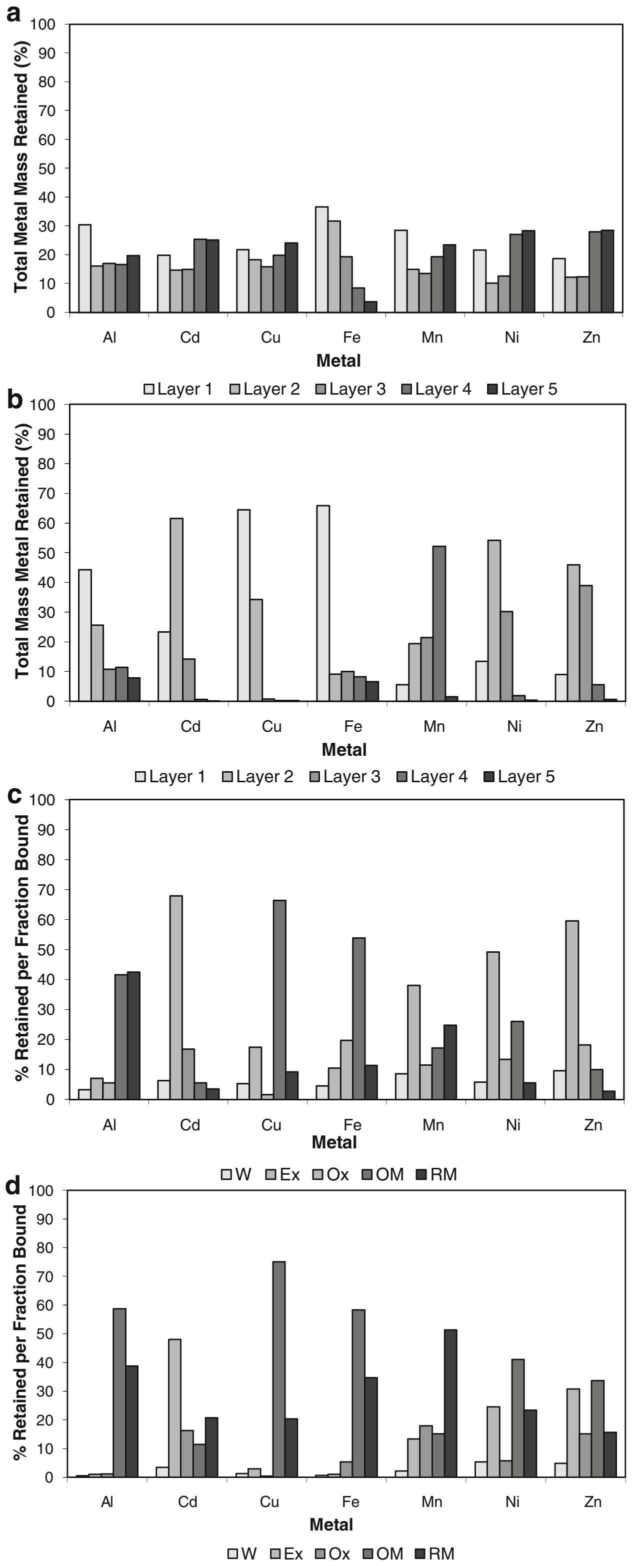

Fig. 7 Metal mass retention in HQ-HC column: per layer at **a** 0°C and **b** 20°C, and per fraction bound at **c** 0°C and **d** 20°C

retention was noted for Al, Zn, Mn, Ni, and Cd, which were primarily associated with the exchangeable fraction (Fig. 7c). At 20°C, the effect of desorption was minimal for most of the metals, which was attributed to the increased association of these metals with the organic matter and residual fractions (Fig. 7d). Cd remained primarily bound to the exchangeable fraction and exhibited breakthrough at 20°C (Fig. 7d), as well as desorption after the addition of the dilute AMD at 20°C (Fig. 1c).

High-Flow Low AMD Concentration: The responses observed for the HQ-LC columns at 0 and 20°C were generally similar to the responses noted in the HQ-HC columns (Fig. 7). The distribution of metals with depth is presented in Fig. 8a and b for the 0 and 20°C cases, respectively. As in the previous cases, Al, Zn, Mn, Ni, and Cd were generally found to be well distributed throughout the depth of the HQ-LC column at 0°C, which is consistent with the observed breakthrough of these metals under these experimental conditions (Fig. 8a). The breakthrough of Cu was not observed in either of the HQ-LC columns (Figs. 1d, 2d). From Fig. 8a and b, it can be seen that Cu was largely retained within the first two layers of the peat columns at 0°C and the first layer of the peat column at 20°C. Under these loading conditions, Fe was also mainly associated with the first layer at both temperatures. However, there appeared to be a significant distribution of Fe in the lower layers of the column as well ($\approx 10\%$). The distribution of Fe in the column was probably due to the initial composition of the peat material (Table 1), rather than the removal of Fe. Figure 8c demonstrates the percentage of metal mass retained per fraction bound at 0°C for the HQ-LC loading condition. No significant change in metal retention trend was noted compared to the HQ-HC columns. At 0°C, Zn, Mn, Ni, and Cd were largely bound to the exchangeable fraction, while Cu and Fe were primarily associated with the organic matter fraction. The metal mass retained per fraction bound at 20°C is presented in Fig. 8d. The gradual recovery of the cumulative metal retention curves noted for Fe, Mn, Zn, and Ni at 20°C (Fig. 2d) suggest the establishment of a sulfate-reducing environment and the start of biologically mediated metal sulfide precipitation, which was confirmed with the rise in effluent pH (Fig. 3b), low effluent DO concentrations, and higher sulfate (Fig. 4b) consumption rates. This was further supported by the fact that Fe, Al, Zn, Mn, Ni, and Cu were highly retained within the organic matter and residual fractions overall (Fig. 8d), particularly in the mid-layers of the column (Fig. 8b). As with the HQ-HC case, the flushing of the columns with the dilute AMD had a much lower effect on metal retention at 20°C than at 0°C (Figs. 1d, 2d). Desorption of Al, Zn, Mn, Ni, and Cd was noted at 0°C (Fig. 1d). At 20°C, on the other hand, the effect of desorption was negligible for most of the metals, with the exception of Cd, for which complete metal breakthrough was observed.

Discussion

Each of the eight columns in the loading study represented a metal mitigation column with a step influent concentration at the start of the experiment, followed by a decrease in concentration and increase in flow step at the end of the experiment. The HQ-HC columns represented moderate strength AMD under operational design flow. The HQ-LC, LQ-HC, and LQ-LC columns could represent seasonal variations in AMD discharge, such as a decrease in AMD generation in the fall due to changes in temperature; a decrease in flow due to summer drought conditions, and; a reduction in flow and AMD generation due to winter temperatures and partial freezing of water. The step decrease in AMD loading and increase in flow would be representative of spring runoff conditions, which could result in desorption of the metals retained in the peat column. Seasonal temperature effects were simulated by conducting the experiment with a set of four columns at 0°C and the other set of columns at 20°C.

Other studies have been conducted which examined the metal sorption capacity of peat and factors that may affect metal removal using peat to treat AMD and metal rich waters under laboratory conditions, either in batch tests or column experiments (Bonnett and Cousins 1987; Champagne et al. 2005; Gosset et al. 1986; Ho et al. 1995; Ringqvist and Oborn 2002; Twardowska and Kyziol 1996). From these studies, it was noted that the heterogeneity of peat types, degree of decomposition, experimental procedures, and operational conditions could influence experimental observations and create difficulties when comparing studies. This was indeed the case in the present study where metal removal mechanisms changed during the experiment, more than likely governed by a flow regime that facilitated biological growth and the establishment of anaerobic zones at 20°C. This effect was more readily observed at higher flow rates.

Effect of Influent Constituent Concentration

The concentration of metals in solution is an important factor in the sorption of metal ions onto peat. Ho et al. (1995) observed that when Ni concentrations increased, the reaction mixture equilibrium pH decreased. This resulted from H^+ being desorbed as Ni was being adsorbed. As such, when Ni concentrations increased, the pH decrease effect was greater and Ni adsorption was less effective. Similar results were reported by Twardowska and Kyziol (1996) for Cr, Cu, Zn, and Cd, and by Ringqvist and Oborn 2002 for Cu and Zn.

In this study, breakthrough occurred in the following order at 0°C: LQ-LC < HQ-LC < LQ-HC < HQ-HC. Sulfate (Fig. 4a) utilization rates, effluent DO concentrations, and pH levels (Fig. 3a) were generally similar at the high and low influent constituent concentrations. The breakthrough of all metals, with the exception of Fe (96.7% retention), was observed in the HQ-HC column (Fig. 1c). For the remaining loading conditions, Cd, Mn, Zn. Al, and Ni breakthrough was noted in all of the columns, with the exception of Cu and Fe which exhibited greater than 97 and 96% retentions, respectively (Fig. 1). Metal retention of Al, Ni, Mn, Zn, and Cd was generally found to be well distributed throughout the peat column at all loading conditions (Figs. 5a, 6a, 7a, 8a). In general, the metal removal efficiency at 0°C was found to be Cd < Mn < Zn < Al < Ni < Cu < Fe. At 20°C, the responses of the columns to influent constituent concentrations differed from that observed in the columns at 0°C. The impact of higher constituent concentrations on the sorption capacity of the peat appeared to be affected by the development of other metal removal mechanisms within the column. Breakthrough (Table 3) was noted for Cd, Mn, Ni, Zn, and Al in the LQ-HC column (Fig. 2a). However, with the exception of Cd, no breakthrough was noted in the HQ-HC column (Fig. 2c). Similarly, under lower influent constituent concentration conditions, metal breakthrough was observed in the LQ-LC (Fig. 2b) and HQ-LC columns (Fig. 2d). However, in both cases, the breakthrough curves exhibited a recovery in cumulative metal retention with volumetric throughput, which would indicate the establishment of other metal removal mechanisms with time.

The removal of Cu, Cd, Ni, and Zn by peat was investigated by Gosset et al. (1986). They observed a selective metal adsorption order where Ni > Cu > Zn ≈ Cd over a pH range of 0–6.5. Similar results were reported by Bonnett and Cousins (1987), where the preferential sorption order was Cu > Fe > Cr > Ni > Al > Zn > Mn at pH values ranging from 2.5 to 5.5. Sorption studies that observed Ni and Cu removal by peat carried out by Ho et al. (1995) corroborate the preferential removal of Cu over Ni. Other studies that observed the affinity of metal sorption onto peat reported the following orders: Twardowska and Kyziol (1996) Cr > Cu > Zn > Cd; Ringqvist and Oborn (2002) Cu > Zn; Champagne et al. (2005) Cu > Fe > Al > Ni > Cd > Zn > Mn. The results of the present study generally corresponded well with these previous studies, where similar selective metal adsorption orders were noted.

As noted in the present study, the pH of the influent solution can affect the metal sorption capacity of peat. Gosset et al. (1986) observed that as pH increased from 0 to 6.5, the percent of Cu, Cd, Ni, and Zn sorbed onto peat increased. In fact, they reported that the percent of Cu, Cd, and Zn sorbed increased from approximately 0 to close to

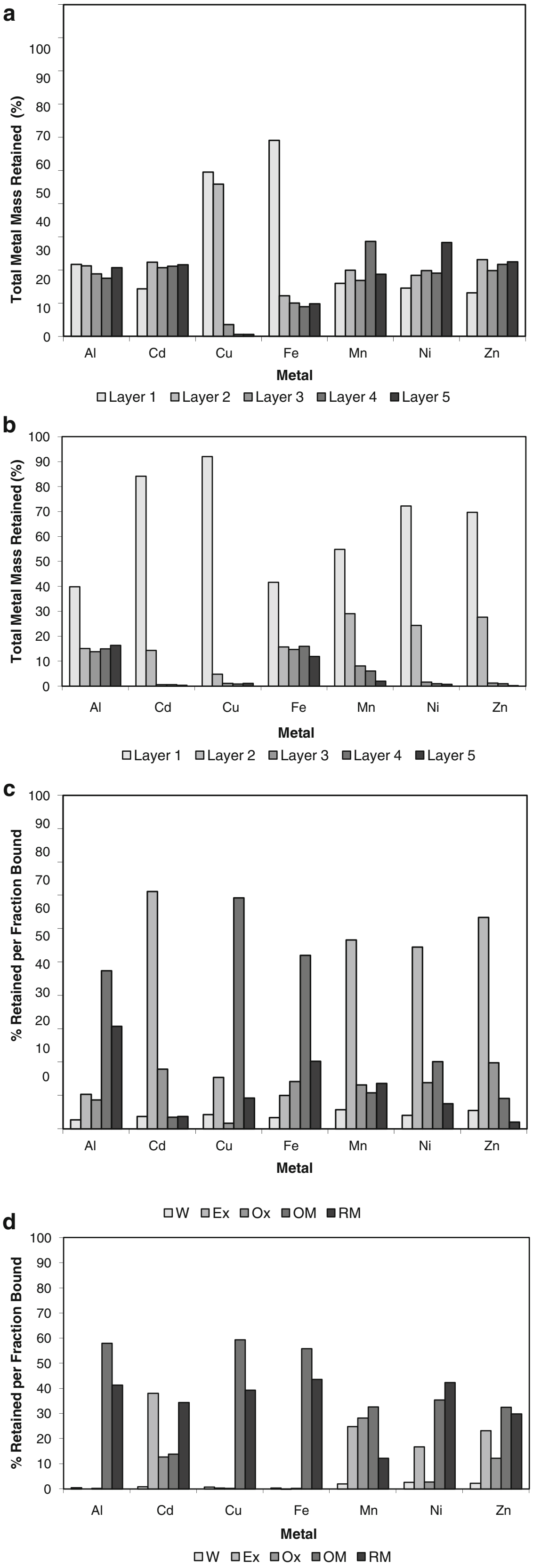

Fig. 8 Metal mass retention in HQ-LC column: per layer at **a** 0°C and **b** 20°C, and per fraction bound at **c** 0°C and **d** 20°C

100% within 4–5 pH units. Bonnett and Cousins (1987) reported similar results for Cu, Fe, Cr, Ni, Zn, Al, Zn, and Mn over a pH range of 2.5–5.5. They also noted that selectivity for metal sorption became less important when the pH was increased to 4.0 and above. This was attributed to an increase in negative sites on the functional groups due to deprotonation. Another observation was that Mn, in comparison to other metals, was significantly less adsorbed, even up to pH 5.5. Similar amounts of metal sorption occurred at pH 4 and 5.5. Ho et al. (1995) studied the sorption of Ni onto peat surfaces over a pH range of 2–7 and reported that similarly, the amount of Ni sorbed increased between pH 2 and 4; however, at pH values between 4 and 7, Ni sorption increased only marginally. Ringqvist and Oborn (2002) studied the sorption of Cu and Zn onto peat at pH values of 4 and 8. They reported that at these pH values, the sorption of Cu was unaffected, though the sorption of Zn increased significantly from pH 4 to pH 8. In fact, the level of Zn sorbed at pH 8 was the same as that for Cu.

Effect of Flow Rate

At 0°C, flow rate was secondary to the effect of AMD constituent concentration. The volumetric breakthroughs of metals for each loading condition are presented in Table 3. In both the high and low AMD constituent concentration cases, metal breakthrough was consistently found to occur more rapidly at the lower flow rate, which did not conform with the expected breakthrough behavior where high-flow breakthrough would have been expected prior to low-flow breakthrough with similar AMD constituent concentrations. This behavior is attributed to a poorer distribution of flow and the consequent establishment of preferential flow paths at lower flow rates, which would lead to a smaller effective volume for metal mitigation within the low-flow columns.

At 20°C, the highest removal efficiencies were also noted in the high-flow columns. This was attributed to the establishment of sulfate-reducing conditions in these columns, where the peat would act as a carbon source and the moderate sulfate concentrations would act as an electron acceptor for sulfate reducers in the column. The development of sulfate-reducing conditions in the high-flow columns was most likely due to the DO concentrations in the peat columns. Under this temperature regime, the solubility of oxygen in water was lower than at 10°C, which, combined with the higher biological kinetics at higher temperatures, would lead to a greater consumption of DO by microorganisms than in the low-temperature columns under identical loading conditions. The opportunity for aeration in the column was also lower than in the low-flow columns because of the higher flow rate and coincident saturation of the peat.

The establishment of sulfate-reducing conditions in the high-flow columns at 20°C was indicated by the relatively low effluent DO concentrations, the higher sulfate removal rates (Fig. 4b), and the significant increase in pH (Fig. 3b). These conditions led to a decrease in effluent metal concentrations via metal sulfide precipitation reactions, resulting in an increased effluent solution pH as a result of alkalinity generation, a product of biologically mediated sulfate reduction. The apparent recovery of the cumulative metal retention curves noted for Fe, Zn, and Cd in the LQ-LC column at 20°C (Fig. 2b) might also suggest the presence of a sulfate-reducing environment. However, this was not supported by an increase in solution pH or sulfate utilization rate, as was observed in the high-flow columns. It is believed that the low-flow systems could also eventually develop substantial bacterial growth, which would lead to higher sulfate and metal removal efficiencies.

The effect of the sulfate-reducing environment was noted more rapidly in the high-concentration column than in the low-concentration column. The HQ-HC (Fig. 2c) system was established more rapidly (19 days) than the HQ-LC (Fig. 2d) system (43 days) due to the higher sulfate concentrations in this column. It is surmised that once a substantial growth of the bacterial system has taken place, higher sulfate utilization rates and greater metal retention would become apparent.

Effect of Temperature

In general, metal adsorption and retention were higher at warmer temperatures. Under the lower temperature regime, the strength of metal association with the exchangeable fraction of the peat (Zn, Mn, Ni, and Cd) appeared to decrease and, hence, metals typically retained within this fraction were retained to a lesser degree. As was previously noted, ion exchange involves the binding of metal ions onto peat functional groups via electrostatic forces in a relatively weak outer-sphere bond, and the metal ion can easily be exchanged by other outer-sphere complex forming ions. This weak ion exchange bond is typically considered to be an endothermic reaction, which would support the results noted in this study. Iron and Cu, on the other hand, demonstrated higher or comparable metal retentions at lower temperatures under most loading conditions. These metals were primarily associated with the organic matter fraction, where adsorption reactions would generally be characterized as exothermic processes, thereby causing a weakening of adsorption forces between the peat binding sites and the Fe and Cu ions (Viraraghavan and Dronamraju 1995) at higher temperatures. The higher temperature conditions also allowed for the development of sulfate-reducing conditions in the high-flow columns as more anaerobic zones were established in the unsaturated columns at higher flow rates. This unexpected phenomenon made it difficult to differentiate between the different metal removal mechanisms under the high flow rate conditions at 20°C. The establishment of sulfate-reducing bacteria consortia was less likely to occur at lower temperatures because these are typically mesophilic organisms.

Effect of Desorption

The flushing of the columns with dilute AMD generally had little impact on retention of Cu and Fe, which were largely associated with the organic matter fraction. Under LQ-HC and LQ-LC loading conditions at 0°C, decreases in cumulative metal retentions were noted for Al, Zn, Mn, Ni, and Cd, which were primarily associated with the exchangeable fraction. Ringqvist and Oborn (2002) investigated the adsorption mechanisms of Cu and Zn. Cu is primarily adsorbed as inner-sphere complexes and Zn as outer-sphere complexes. Their study suggested that the affinity of a metal ion for sorption by peat is related to its interaction mechanism, with inner-sphere complex forming metals being preferred. Sequential fractionation of bound metals carried out by Twardowska and Kyziol (1996) indicated that Cr was most preferentially bound to peat and that most of the Cr removed was strongly bound to the organic fraction, indicating the formation of inner-sphere complexes. Zn and Cd were the least preferred metal ions adsorbed by peat, and a large amount of these metals were bound to the exchangeable fraction, indicating that they were weakly bound via ion exchange mechanisms related to outer-sphere complexes. Similar binding relationships were noted in this study, where metals exhibiting a higher retention within the peat (Cu and Fe) were primarily associated with the organic fraction, while those metals associated with the exchangeable fraction (Ni, Zn, Mn, and Cd) were generally more mobile within the peat and experienced breakthrough, This effect was generally less evident at 20°C. In the HQ-HC and HQ-LC columns, a decrease in the cumulative metal retention of Al, Zn, Mn, Ni, and Cd was also observed at 0°C during the desorption phase. At 20°C, desorption was negligible for all of the metals, with the exception of Cd, which was attributed to the increased association of these metals with the organic matter and residual fractions. Cd did not show a strong affinity for the organic matter fraction, and thus, breakthrough and desorption were noted at 20°C.

Conclusions

The column sorption/desorption study demonstrated the effect of flow rate, AMD constituent concentrations, and temperature on metal retention in packed peat columns operated in an unsaturated flow regime. At 0°C, it appeared as though the association of metals typically bound with the exchangeable fraction of the peat (Zn, Mn, Ni, and Cd) weakened and the metals were retained to a lesser degree. Fe and Cu, which were primarily associated with the organic matter fraction, demonstrated higher or comparable mass retentions at lower temperatures under most loading conditions. At 0°C, the breakthrough of metals generally occurred in the following order: LQ-LC < HQ-LC < LQ-HC < HQ-HC with a metal removal efficiency of Cd < Mn < Zn < Al < Ni < Cu < Fe. At 20°C, the highest removal efficiencies were noted in the high-flow columns.

The combination of increasing pH, low effluent DO (<2 mg/L), and high sulfate utilization rates indicated the presence of anaerobic biological activity in the high-flow columns at 20°C, where less refractory organic fraction of the peat could act as the carbon source necessary for sulfate reduction to occur. The establishment of sulfate-reducing conditions is largely a function of DO availability, which depends on the rate of reaeration in the peat column and the solubility of DO, where DO solubility decreases with increasing temperature. It was presumed that more rapid biological kinetics at higher temperatures led to a greater consumption of DO by microorganisms. The rate of reaeration was also expected to be lower at higher flow rates resulting from the more saturated conditions within the column and hence, creating less opportunity for gas-phase diffusion, facilitating the establishment of a greater volume of anaerobic zones within the columns. These conditions led to a decrease in effluent dissolved metal concentrations due to metal removal via other removal processes including biosorption onto the growing biofilm and metal sulfide precipitation, as was indicated by the increased retention of metals in the residual fraction under the high flow conditions. Effluent solution pH also increased due to the biologically mediated, alkalinity-generating sulfate reduction. The absence of microbiological activity at 0°C was probably due to the reduced kinetics of biological reactions at colder temperatures. Under sulfate reducing conditions, the primary metal removal mechanism would become metal sulfide precipitation. The increased pH resulting from sulfate reduction could also promote the precipitation of metal carbonates. The establishment of a sulfate-reducing environment, though unintended in this experiment, was found to be important for the removal of metal ions typically associated with the exchangeable fraction (Ni, Mn, and Zn) and relatively mobile through the peat biofilter, with the exception of Cd, which remained mobile through the system. However, the establishment of sulfate-reducing conditions in the peat biofilter component requires a biodegradable carbon source. In the absence of an external carbon supply, the peat would act as a carbon source, which could lead to the deterioration of the peat biofilter matrix.

It is important to note that peat naturally has an acidic nature, and effluents exiting peat biofilters tend to be acidic. Further, peat is not capable of reliably removing all metal ions for an extended operational period without requiring the replacement of the biosorbent material. As a result, peat biosorbent systems are not recommended as stand alone treatment alternatives. Peat biofilters should be used in combination with an alkalinity producing system, such as limestone, or if further metal removal is required, a sulfate reducing bacteria bioreactor could be employed.

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