Poorly humified peat as an adsorbent for metals in wastewater

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Received 15 May 2000; received in revised form 23 August 2001; accepted 21 September 2001

Abstract

Metal adsorption and surface charge determinations were performed previously on well-characterised *Sphagnum* and *Carex* peat samples. The aim of this investigation was to determine metal adsorption from complex wastewaters onto these peat samples and compare it to the adsorption onto peat granules, clinoptilolite, glauconite and a flue dust from steel production. A sulphide mine leachate, a landfill leachate and a laundry wastewater were chosen, giving a variation in pH, ionic strength, total organic carbon and concentrations of metals. Metal adsorption was determined in batch and column experiments. The wastewater composition was of great importance for metal removal efficiency, mainly due to the difference in dominating metal species. In the sulphide mine leachate, containing free metal ions, a high metal adsorption was observed onto both peat and inorganic adsorbents. In the landfill leachate the metals formed carbonate and organic complexes and a low metal removal was achieved. Contrary to the leachates, the laundry wastewater contained suspended particles. The high amount of metals removed, 80% of the Cu and 30–60% of the Zn concentration, was probably withdrawn bound to the particle fraction. The highest removal of metal ions was obtained in the sulphide mine leachate with *Carex* peat, removing 97–99% of the Zn and 85–100% of the Cu content. The *Sphagnum* peat sample removed 37–77% of the Zn and 80–100% of the Cu content. The differences found between *Sphagnum* and *Carex* peat were attributed to the original chemistry of the plant material and the habitat conditions at the time of peat formation. Generally, the combination of glauconite or clinoptilolite with the peat samples in column experiments gave a minor improvement in metal removal. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: *Sphagnum* peat; *Carex* peat; Wastewater; Heavy metals; Adsorption

1. Introduction

Sources of heavy metal contamination can be found in landfills and mine waste deposits, from which metals can leach for very long periods of time. Peat is a cheap product which is available in many areas, and which has the ability to adsorb heavy metals. Metal adsorption from municipal, industrial and mine deposits onto peat have been investigated previously [1–6]. Lidkea [3]

reports an adsorption capacity of 48 mg g⁻¹ for fibric (mainly *Sphagnum*) peat. Rock et al. [4] write “peat seems to have a great potential in the treatment of heavy metals, pesticides, and other toxic materials and may be especially adaptable to the treatment of leachate”. That authors also found that leachate odour was decreased after filtration through peat. Problems with clogging during filtration of municipal leachate have been reported by McLellan and Rock [7] and Lyons and Reidy [6]. Parameters influencing metal adsorption from wastewater are metal concentration in the solution, ionic strength, pH, and complex-forming substances. Mechanisms other than adsorption, such as precipitation

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and mechanical entrapment, are involved in treating complex wastewaters [1,2]. Previously it was found that *Sphagnum* peat adsorbed a higher amount of Cu compared to *Carex* peat at pH 4.7 [8]. The surface charge density was found to be higher on *Sphagnum* peat than on *Carex* peat in the pH interval 4.5–5.5 [9]. It was further found that absorption of Zn in particular but also of Cu increased more with the pH value on *Carex* peat than on *Sphagnum* peat, giving a higher metal adsorption onto *Carex* peat at high pH values [10].

Fine dust, produced in large quantities in the steel production at SSAB in Luleå, has been found to be a potential adsorbent for metals. Copper, lead, zinc, cadmium and chromium were removed from solutions by surface adsorption in the pH range 5.5–11.5 [11]. The natural zeolite, clinoptilolite, is used in applications such as chemical filters, odour control and filters for municipal and drinking water. Clinoptilolite adsorbs ammonium ions from leachate [12], but also metal ions [13,14]. Glauconite, a three-layer sheet aluminosilicate, has been found to reduce heavy metal cations, lessen unpleasant odour and diminish murkiness of landfill leachate [15,16].

Metal adsorption [8,10], and surface charge determinations [9] have previously been performed on well-characterised [17] *Sphagnum* and *Carex* peat samples. The aim of this investigation was to determine metal adsorption from complex wastewaters onto these peat samples and compare it to the adsorption onto peat granules and inorganic adsorbents, i.e. clinoptilolite, glauconite and a residue from steel production. A sulphide mine leachate, a landfill leachate and a laundry wastewater were chosen, giving a variation in

pH, ionic strength, total organic carbon and metal concentrations.

2. Materials

2.1. Adsorbents

Sphagnum and *Carex* peat samples previously used in metal adsorption experiments [8,10] and surface charge determinations [9] were used in this study (Table 1). The samples were untreated in this study and in studies performed by Fattahpour Sedeh [8] and Bergner et al. [9] while acid washed samples were used by Ringqvist and Öborn [10]. Poorly humified peat samples, humification degree 2–4 according to the von Post scale (ranging from 1 to 10), were chosen. Poorly humified peat has a coarser structure than highly humified peat, which gives sufficient permeability in column experiments. The botanical origin of the peat samples was previously found [9,8] to be more important for metal adsorption than the humification degree. Two *Sphagnum* peat samples of different sections, and one *Carex* peat sample (Table 1) were chosen in this study. A peat pellet with unknown botanical origin and humification degree was used as well. The *Sphagnum* peat samples chosen were peat formed by the *Sphagna* sect. *Cuspidata*, growing in pools or in very low areas on the mire and the *Sphagna* sect. *Acutifolia*, forming hummocks. A higher CEC in the *Acutifolia* group of *Sphagnum* mosses has been reported compared to the *Sphagna* sect. *Cuspidata*. The difference was correlated to the uronic acid content in the moss [19,20]. The same pattern has also been

Table 1
Peat samples used in the experiments^a

	<i>Sphagna</i> sect. <i>Acutifolia</i> peat	<i>Sphagna</i> sect. <i>Cuspidata</i> peat	<i>Carex</i> peat
Sample code	SF06	Su39	AD04
Botanical composition (%)	S ₉₂	N ₅ Gr ₁₀ S ₈₂	C ₉₈
Composition of <i>Sphagna</i> (%)	Pa ₁₀ Ac ₆₆	Cu ₇₄	—
Humification degree (von Post)	3	2–3	2–3
Ash content (% of dry matter)	1.2	1.5	6
Uronic acid (%)	14–17	not measured	6
Klason lignin (%)	18–29	39	53–56
Fe (mmol kg ⁻¹)	31	36	290
Ca (mmol kg ⁻¹)	41	80	175
Cu (mmol kg ⁻¹)	<0.13	0.04	0.05
Zn (mmol kg ⁻¹)	0.09	0.08	0.04
Surface charge, Bergner et al. [9], (mmol(+) g ⁻¹)	0.48	0.38	0.12
Langmuir equation for Cu adsorption, Fattahpour Sedeh [8]			
Constant	0.0589	not measured	0.0316
(x/m) _{max} (mg g ⁻¹)	42.6	not measured	30.2

^aS = *Sphagnum* mosses, Pa = *Sphagna* sect. *Palustris*, Ac = *Sphagna* sect. *Acutifolia*, Cu = *Sphagna* sect. *Cuspidata*, N = *Ericaceous* dwarf shrubs, Gr = *Poaceae* and herbaceous plants, C = *Cyperaceae* (e.g. *Carex* spp.); botanical composition according to Bohlin [18]; index are percentage contained in the sample.

observed in peat [21]. Further description of the peat samples used in this investigation can be found elsewhere, using the sample codes [22]. Due to different demands on the habitat for the peat-forming plants, *Carex* peat generally has higher ash content than *Sphagnum* peat (Table 1).

Inorganic adsorbents included for comparison with the peat were clinoptilolite, glauconite and a residue from steel production at SSAB in Luleå. The SSAB residue consists of flue dust collected in scrubbers in the wet gas cleaning plants. About 84 000 tonnes are produced every year in Sweden. The dust contains 57% Fe, 12% CaO and 3% MgO, with the most prevalent phase of Fe in the form of FeO [11]. An untreated sample of the natural zeolite clinoptilolite, 80% purity, as well as an untreated sample of the three-layer sheet aluminosilicate glauconite were used in the study.

2.2. Wastewater

The wastewaters used were leachate from an industrial landfill, leachate from a mining area, and wastewater from a laundry (Table 2). The industrial landfill Dåvamyran, situated near Umeå, has been used since 1974 for industrial and building refuse as well as ash and cinder. Samples were collected in December 1995 and in December 1996. The landfill leachate was characterised by a high ionic strength and relatively low heavy metal content and a pH value of 7.8. All batch experiments were performed with the sample collected in 1995, while the column experiments were performed with the sample collected in 1996. The mining leachate originated from Laver, a closed copper mine in northern Sweden, where mining activities started in 1936 and ended in 1946. Around 1.2 million tonnes of tailings were deposited close to the mine [24]. Leachate was collected in 1995.

Table 2

Initial concentration (mg L^{-1}) of main elements and heavy metals in leachate from the sulphide mine area Laver (samples collected in Dec 1995), Dåvamyran landfill (samples collected Dec 1995 and Dec 1996) and wastewater from the KM-laundry in Gammelstad (samples from two occasions in Dec 1995)

	Sulphide mine leachate	Landfill leachate		Laundry wastewater	
		Dec 1995	Dec 1996	Sample 1	Sample 2
Ca	13.5	173	247.2	51.1	13.1
Fe	0.8	2.2	3.5	6.98	5.25
K	1.7	652	679	26.8	9.0
Mg	2.3	59.6	49.6	8.4	2.3
Na	2.3	1145	1140	839	362
Al	0.3	0.2	0.01	3.35	2.74
Mn	0.4	0.2	0.3	0.187	0.161
Ba	0.01	0.2	—	0.309	0.086
Zn	298×10^{-3}	53.5×10^{-3}	94.7×10^{-3}	1650×10^{-3}	1080×10^{-3}
Cu	70.9×10^{-3}	21.6×10^{-3}	45.0×10^{-3}	1210×10^{-3}	715×10^{-3}
Co	2.9×10^{-3}	7.4×10^{-3}	8.4×10^{-3}	11.7×10^{-3}	7.41×10^{-3}
Ni	3.4×10^{-3}	39.1×10^{-3}	56.2×10^{-3}	132×10^{-3}	88.6×10^{-3}
Cr	$<0.500 \times 10^{-3}$	25.4×10^{-3}	54.2×10^{-3}	210×10^{-3}	141×10^{-3}
Cd	0.8210^{-3}	0.7×10^{-3}	0.6×10^{-3}	11.0×10^{-3}	5.40×10^{-3}
Pb	0.6×10^{-3}	3.1×10^{-3}	2.4×10^{-3}	424×10^{-3}	233×10^{-3}
Hg	$<0.200 \times 10^{-3}$	0.25×10^{-3}	n.m.	1.38×10^{-3}	$<3.00 \times 10^{-3}$
Total metal cations	21	2032	2120	940	397
S	27.4	67.2	111.2	37.2	36.8
P	0.13	0.84	0.29	—	—
TOC ^a	7.3	624	264	—	2027
N-tot			130		
NH ₄ -N			100		
Cl ⁻	5.6 ^b	1100 ^c			
HCO ₃ ⁻		1000 ^c			
pH	5.7	7.8			10.8

^aTotal organic carbon.

^bConcentration in an average river water [23].

^cAnnual mean value.

The leachate from the copper sulphide mine area contained elevated concentrations of Zn and Cu compared to uncontaminated stream water and the pH value was 5.7. However, the metal concentrations were low related to leachates from other acid mine areas (e.g. [25,26]). Wastewater was collected from the KM laundry in Gammelstad after washing of overalls used by mine workers from LKAB in 1995. Samples were collected on two different occasions. The wastewater had a high concentration of heavy metals and a high pH value, 10.8. A summation of all measured cationic ions gave about 20 mg L^{-1} in the sulphide mine leachate, about 2000 mg L^{-1} in the landfill leachate and 400 or 950 mg L^{-1} in the laundry wastewater (Table 2). The concentration of total organic carbon (TOC) was 2000 mg L^{-1} in the wastewater from the laundry, 260–620 mg L^{-1} in the landfill leachate and 7 mg L^{-1} in the leachate from the mine deposit.

3. Methods

3.1. Batch experiments

Adsorbent and wastewater were mixed in batch experiments in acid-washed 250 mL glass bottles placed on a shaker for 1 week at room temperature. After filtration through a $45 \mu\text{m}$ glass fibre filter, the effluent was collected and analysed for metals and TOC. Amount of adsorbent added to 100 mL wastewater was 40 g L^{-1} except for the peat granules, where 20 g L^{-1} was used. The amounts of metals leached from the adsorbents in distilled water were determined with the same method. In metal concentrations given after contact with the adsorbents in the batch experiments, the amounts of metals leached in distilled water were deducted.

3.2. Column experiments

In the column experiments a glass column, i.d. 30 mm, with a plastic net at the bottom covered with a glass fibre filter, was used. Experiments were performed with peat

samples alone or in combination with glauconite or clinoptilolite. Peat particles smaller than $45 \mu\text{m}$ were removed through a sieve. The adsorbents were placed into the columns, 0.5 g peat with a height of approximately 3.0 cm or 3.0 g mineral giving a height of approximately 0.5 cm, covered by 0.5 g peat. A glass fibre filter was placed above the peat surface. Sulphide mine leachate and landfill leachates, respectively, were percolated through the peat or peat/mineral filter. No column experiments were performed with the laundry wastewater, since pre-experiments showed that it caused the peat bed to clog. The water flow was regulated to achieve a contact time of 20 min. The effluent was collected in $4 \times 25 \text{ mL}$ fractions, giving a total volume of 100 mL, which correspond to 5 bed volumes. This volume is enough to describe the metal removal efficiency of the peat and peat/mineral samples.

3.3. Metal analysis

Metal concentrations were measured with ICP-AES or ICP-MS technique after acidification with nitric acid (1 mL per 100 mL). The samples were analysed by two laboratories, SGAB in Luleå and the Environmental Research Laboratory at the Department of Forest Ecology, SLU in Umeå. The metal analyses at the laboratories were compared for the initial metal concentrations in the landfill and sulphide mine leachate samples collected in 1995 and the deviation was found to be minor. In samples measured by SGAB, the deviation was given for each analysis (Table 3). A deviation of <5% for all elements was given for samples analysed by the Environmental Research Laboratory. Nitrogen analyses were conducted for the landfill leachate samples at the Laboratory for Chemistry and Biomass at SLU in Umeå.

3.4. Speciation calculations

Calculations of the speciation of Cu, Zn, Ni, Cd and Pb in the wastewaters were performed using the chemical equilibrium model WHAM-W [27]. Initial metal and sulphur concentrations presented in Table 2

Table 3
Percentage of error in analyses of filtrates from the batch experiment performed by SGAB

	Cu	Zn	Ni	Cd	Pb	Cr
<i>Sphagnum Acutifolia</i> peat	1–3	1	1–18	6–9	0–4	9
<i>Sphagnum Cuspidata</i> peat	1–5	1–2	2–4	7–25	1–5	1
<i>Carex</i> peat	1–4	1–4	2–8	6–14	4–11	6
Glauconite	1–5	0.1–8	2–6	4–11	2–4	1–4
Clinoptilolite	1–3	3–7	2–15	7–46	2–5	2
SSAB flue dust	1–12	5–16	2–8	3–12	2–5	2

were used in the calculations. All sulphur was assumed to occur as SO_4^{2-} . The CO_2 pressure of the atmosphere, $10^{-3.5}$ atm, was used in the calculations for the sulphide mine and laundry wastewater. Nitrogen and TOC were not included in the calculations. Both NH_3 and organic acids present in the wastewaters can form complexes with the metal ions. Therefore, a speciation including these elements was performed for the landfill leachate, having a high nitrogen and TOC concentration. The composition of the TOC fraction was unknown but acetic acid is one of a large number of different organic compounds found in large quantities in some landfill leachate samples [28]. A speciation of Cu and Zn in a solution of Cl^- , SO_4^{2-} , HCO_3^- , N-tot and acetic acid was performed at varying acetic acid concentrations, using the programme SOLGASWATER [29]. Concentrations according to the concentration in the landfill leachate (Table 2) were used in the calculations.

4. Results

4.1. Speciation of metal ions

According to the speciation calculations, the metal ions are mainly found as aquo complexes ('free metal ions'), $\text{M}_x(\text{H}_2\text{O})_y^{n+}$ in the sulphide mine leachate but occur as metal complexes in the landfill leachate and laundry wastewater (Table 4). In the landfill leachate metal carbonate complexes dominated, while a minor part of the metals occurred as free ions. Copper and zinc should occur to a high extent as positively charged

complexes with HCO_3^- according to the calculation presented in Table 4. A speciation of the landfill leachate including nitrogen and acetic acid showed that the main part of the nitrogen occurred as ammonium ions and only a minor part formed NH_3 complexes with the metals. At low concentration of acetic acid Cu and Zn formed carbonate complexes, while at high concentrations organic acid complexes dominated (Fig. 1). No free Cu ions were available according to the calculation, while Zn occurred to some extent as free ions. In the laundry wastewater, which had a high pH and TOC, a very brief calculation of the speciation, without organic material, showed that all metal ions except Cd should occur as metal hydroxides or carbonates.

4.2. Batch experiments

The total metal removal varied between the different wastewaters tested (Fig. 2). The removal of metals was low with all adsorbents in the landfill leachate, while a higher removal was achieved in the sulphide mine leachate and the laundry wastewater. The landfill leachate with its high pH and ionic strength seems to have dissolved metals initially bound to the adsorbents.

In the sulphide mine leachate, where the metal ion occurred to a high extent as free ions, a high removal of Cu was reached with all adsorbents tested according to Table 5. Zinc was also removed to a rather high extent (Table 5). The pH value in the sulphide mine leachate, initially pH 5.7, decreased when the leachate was mixed with the peat samples. At the end of the experiment, pH had decreased to 3.6 with the *Sphagna* sect. *Cuspidata*

Table 4

Metal speciation (%) in wastewater calculated by the programme WHAM-W [27]^a

Sulphide mine leachate		Landfill leachate		Laundry wastewater	
Cu^{2+}	88	Cu^{2+}	1	Cu^{2+}	0
CuHCO_3^+	4	CuHCO_3^+	57	$\text{Cu}(\text{CO}_3)_2$	100
CuSO_4	9	CuCO_3	38		
		$\text{Cu}(\text{CO}_3)_2$	4		
Zn^{2+}	90	Zn^{2+}	19	Zn^{2+}	0
ZnSO_4	10	ZnCO_3	14	$\text{Zn}(\text{OH})_2$	46
		ZnHCO_3^+	65	ZnCO_3	53
Ni^{2+}	91	Ni^{2+}	6	Ni^{2+}	0
NiSO_4	9	NiCO_3	50	NiCO_3	100
		NiHCO_3^+	43		
Cd^{2+}	88	Cd^{2+}	41	Cd^{2+}	21
CdSO_4	11	CdCl^+	54	CdOH^+	34
CdCl^+	1	CdCl_2	4	$\text{Cd}(\text{OH})_2$	45
Pb^{2+}	77	Pb^{2+}	0	Pb^{2+}	0
PbSO_4	22	PbCO_3	88	$\text{Pb}(\text{CO}_3)_2^{2-}$	100
		$\text{Pb}(\text{CO}_3)_2^{2-}$	11		

^a The initial concentrations according to Table 2 were used.

Fig. 1. Distribution of Cu and Zn species at increased concentration of acetic acid in landfill leachate calculated by the program SOLGASWATER [29]. The concentrations of Cu, Zn, S, HCO_3^- and Cl^- according to Table 2 were used in the calculations. (a) Cu, (b) Zn.

peat, 4.2 with the *Sphagnum* sect. *Acutifolia* peat, and 4.9 and 5.0 with *Carex* peat or peat granules, respectively. The peat granules broke up into small particles in the experiment. The pH value increased to pH 7.2 with glauconite, to 7.3 with clinoptilolite and to 10.3 when the leachate was mixed with flue dust.

Generally, a rather low metal removal was achieved in the landfill leachate (Fig. 2). The pH value remained at the same level for all adsorbents, due to a high buffering capacity of the leachate. Copper was adsorbed onto the peat samples, while Zn was released from the *Sphagnum*

Fig. 2. Metal concentration in wastewater before and after contact with different adsorbents at wastewater/adsorbent ratio 40 g L^{-1} (with exception for peat pellets 20 g L^{-1}). The amount metal leached from the adsorbents in distilled water were withdrawn.

peat and the peat granules (Table 5). A high Pb and Cd removal was achieved in particular using the *Carex* peat and peat pellet. No metal removal occurred with clinoptilolite.

In the laundry wastewater, a high Cu removal and a lower Zn removal was achieved with the peat samples, while the inorganic samples gave a high Zn removal and a low Cu removal (Table 5). A high removal of Cd, Pb and Cr was observed with both peat and inorganic samples.

Table 5

Metal removal (%) in batch experiments with 40 g L⁻¹ organic and inorganic adsorbents

	Sulphide mine leachate				Landfill leachate					Laundry wastewater (sample 1)					
	Cu	Zn	Ni	Cd	Cu	Zn	Ni	Cd	Pb	Cu	Zn	Ni	Cd	Pb	Cr
<i>Sphagnum Acutifolia</i> peat	86	38	—	56	32	—	55	37	41	84	65	60	93	95	81
<i>Sphagnum Cuspidata</i> peat	100	67	68	97	86	—	27	62	65	87	35	15	43	87	79
<i>Carex</i> peat	100	99	100	93	68	89	28	72	83	81	60	56	13	81	74
Peat granules ^a	85	67	77	100	—	—	27	81	80	76	31	38	88	88	65
Clinoptilolite	80	98	—	47	—	—	—	—	—	38	97	47	80	97	70
Flue dust	87	100	—	4	—	90	50	0	100	21	99	50	80	98	68
Glauconite	90	98	—	39	6	56	—	20	88	23	58	35	29	88	49

^a Amount of adsorbent used was 20 g L⁻¹. Metal release in distilled water not measured. Sample 2 of the laundry wastewater used.

4.3. Column experiments

The *Carex* peat sample removed 88–97% of Cu, Zn, Ni and Cd, while the *Sphagnum* peat sample removed 70–80% (Fig. 3). A higher amount of Fe was removed using the *Sphagnum* peat sample compared to the *Carex* peat sample. A slight improvement in metal removal was achieved by treating the sulphide mine leachate with *Sphagnum* peat combined with glauconite in the column experiment (Table 6). The TOC concentration decreased when the *Sphagnum* peat sample was used, while out-wash of TOC occurred from the *Carex* peat sample. In the sulphide mine leachate, the *Sphagnum* peat sample adsorbed twice the amount of cations that was adsorbed by the *Carex* peat sample (Table 7) but the cations adsorbed were mainly Ca ions.

In the landfill leachate, the Cu concentration was reduced by 20% after treatment with *Sphagnum* peat (Fig. 4). Zinc was initially released from the *Sphagnum* peat surface but then the concentration decreased by about 50% in the column experiment. Cadmium was released from the *Sphagnum* peat. The concentration of TOC remained unchanged. Only a minor improvement or no improvement at all, in the metal adsorption was achieved with the combination of *Sphagnum* peat with glauconite, or clinoptilolite to the peat sample. The total amounts of adsorbed cations were slightly higher onto the *Sphagnum* sect. *Acutifolia* peat sample, 1.7 mmol g⁻¹, compared to the *Sphagnum* sect. *Cuspidata* peat sample, 1.6 mmol g⁻¹ (Table 7). The difference depended on a higher adsorption of Ca²⁺ to the *Sphagnum* sect. *Acutifolia* peat sample.

5. Discussion

5.1. The sulphide mine leachate

The metal ions mainly occurred as free metal ions in the sulphide mine leachate according to the speciation

calculated (Table 4). Pettersson et al. [30] examined the metal speciation in surface water rich in humic and fulvic acids downstream from a deposit with sulphide mine waste. They found that Zn and Cd predominantly existed as free ions and minor fractions as neutral sulphate and carbonate complexes. Cu was found to form humic and fulvic complexes except at low pH and high concentrations of Al and Fe, where the humic and fulvic acid sites were occupied by trivalent Al and Fe ions. Generally, a high metal removal was reached with all adsorbents tested in the sulphide mine leachate in the present study (Fig. 2). A model describing Cu and Zn adsorption onto *Sphagnum* and *Carex* peat at various pH values and ionic strength (Ca and Na concentrations) determined in a factorial experiment [10] predicted a high Cu and lower Zn removal in the sulphide mine leachate. The reason for the predicted Zn removal being lower than that obtained was probably due to a higher competition between Cu and Zn for adsorption sites in the factorial experiment than in the leachate due to the lower amount of adsorbent used (1.7 g L⁻¹ compared to 40 g L⁻¹).

A higher Zn removal was obtained with *Carex* peat (99% in batch and 97% in column experiments) than with *Sphagnum* peat (38–67% in batch and 77% in column experiments). The removal of Zn was found to increase significantly with pH [10]. The pH value in the *Sphagnum* peat batches was low, between 3.4 and 4.2, while it was nearly 5 in the *Carex* peat sample. However, a higher Cu adsorption capacity of untreated samples of *Sphagnum* peat compared to *Carex* peat was found at pH 4.7 [8]. The higher Zn adsorption onto *Carex* peat compared to *Sphagnum* peat can probably be explained by the higher pH value in the *Carex* peat batches. The result could also indicate a higher affinity for *Carex* peat. A lower adsorption of Zn in particular was found for the *Sphagnum* sect. *Acutifolia* peat, giving a lower pH in the batches compared to the *Sphagnum* sect. *Cuspidata* peat (Table 5). The adsorption of Cu onto peat was found to be less dependent on pH than the adsorption of

Fig. 3. Removal (%) of Ni, Cu, Zn, Cd, Fe and Ca in the sulphide mine leachate in column experiments. (a) *Sphagnum Cuspidata* peat, (b) *Carex* peat.

Zn [10]. In the sulphide mine leachate, the adsorbed amount of Cu was almost the same onto the *Sphagnum* and *Carex* peat samples. Removal rates obtained were 100% in batch and 80–85% in column experiments.

In this study, poorly humified *Carex* peat was a better adsorbent for heavy metals than poorly humified *Sphagnum* peat, while the *Sphagnum* peat sample adsorbed a higher amount of Ca (Table 7). Calcium ions preferentially form complexes with ligands containing oxygen as a donor atom, while Zn ions co-ordinate

preferentially with ligands containing N, P or S as donor atoms [31]. A higher uronic acid content and a lower N, P and S content has been found in *Sphagnum* peat than in *Carex* peat. The *Carex* peat sample initially contained a higher total amount of Ca and Fe (Table 1). Exchangeable Ca ions can more easily be replaced by heavy metals compared to hydrogen ions [32,33]. A lower removal of Ca and Fe was reached in the column experiment with *Carex* peat than with *Sphagnum* peat (Fig. 3).

Adsorption isotherms for Cu, Zn, Ni, Cd and Fe in mixture were determined previously [8] onto the *Sphagnum* sect. *Acutifolia* peat sample. The adsorbed amount of these ions in the column experiment (not achieving maximum adsorption) was about 1/10 of the amount predicted for each metal (Table 7).

5.2. The landfill leachate

The calculation of the speciation of Cu and Zn in the landfill leachate showed that most of the metals in the leachate occurred as carbonate complexes or were bound to the organic fraction in the leachate. The carbonate complexes formed were to a high extent positively charged (Table 4). At increased concentration of acetic acid, used as an example of organic compounds found in landfill leachates, a higher amount of organic acid complexes were formed while the amount of carbonate complexes decreased. A lower metal adsorption was achieved in the sulphide mine leachate with all adsorbents tested in both batch (Fig. 2) and column experiments (Table 6). The reason was most probably that the metal ions to a high extent were bound to the organic fraction in the leachate. High Na concentration and high ionic strength in the landfill leachate can also contribute to a low metal adsorption, due to competition with the heavy metals for adsorption sites.

In the column experiment, Zn was initially released from the *Sphagnum* peat surface but later the concentration decreased by about 50% in the wastewater. In the batch experiment too, Zn was released from the *Sphagnum* peat samples, while the *Carex* peat sample adsorbed Zn to a high extent. Zinc has previously been observed [1] to be exchanged by other ions in treating landfill leachate with peat. Ringqvist and Öborn [10] found that Zn was bound to *Carex* peat to a higher extent than to *Sphagnum* peat at the pH and Ca and Na concentrations prevailing in the landfill leachate. A minor increase in metal removal was obtained in the column experiment adding clinoptilolite or glauconite to the peat sample.

In the column experiment a slightly higher total cation adsorption was reached onto *Sphagnum* sect. *Acutifolia* peat compared to onto *Sphagnum* sect. *Cuspidata* peat (Table 7), earlier found to have a higher metal adsorption capacity [34]. The total amount of cations

Table 6

Metal and TOC removal (%) in column experiments with sulphide mine and landfill leachate, when approximately 5 bed volumes (100 mL) leachate had passed through the column

Metal ion	Sulphide mine leachate				Landfill leachate			
	<i>Sphagnum Cuspidata</i> peat	<i>Sphagnum Cuspidata</i> peat and glauconite	<i>Carex</i> peat	<i>Carex</i> peat and clinoptilolite	<i>Sphagnum Acutifolia</i> peat	<i>Sphagnum Acutifolia</i> peat and glauconite	<i>Sphagnum Acutifolia</i> peat and clinoptilolite	<i>Sphagnum Cuspidata</i> peat
Fe	51	47	10	23	55	45	59	50
Zn	77	94	97	98	55	46	53	56
Cu	80	92	85	86	21	20	41	15
Ni	70	91	88	97	15	19	37	17
Cd	75	88	88	88	−50	−17	23	−33
TOC	10	9	−72	0	2	11	—	2

Table 7

Amount of cations adsorbed onto peat (mmol kg^{−1}) in column experiments, when approximately five bed volumes (100 mL) of leachate had passed through the column

	Sulphide mine leachate				Landfill leachate			
	<i>Sphagnum</i> sect. <i>Cuspidata</i> peat		<i>Carex</i> peat		<i>Sphagnum</i> sect. <i>Cuspidata</i> peat		<i>Sphagnum</i> sect. <i>Acutifolia</i> peat	
	Adsorbed	Released	Adsorbed	Released	Adsorbed	Released	Adsorbed	Released
Ca	39.9		13.7		573.9		648.7	
Na		21.8		7.0	695.9		739.4	
K		1.3	1.3		306.9		255.8	
Mg		14.0		6.2	41.2		82.3	
Fe	1.4		0.5		7.2		7.2	
Mn	1.6		1.1		0.95		1.0	
Al	0.7		1.1		0.11		0.03	
Total ^a	43.7	37.0	17.7	13.1	1 626		1 734	

^aTotal amount of metal cations adsorbed released.

adsorbed agreed rather well with maximum metal adsorption (51 mg g^{−1}) according to the Langmuir isotherm determined in a mixed solution of Cd, Cu, Fe, Ni and Zn for the *Sphagnum* sect. *Acutifolia* peat sample [8]. Lidkea [3] reported the same level (55 mg g^{−1}) for metal adsorption from a landfill leachate onto *Sphagnum* peat. Only a minor correlation between adsorption isotherms and column studies with landfill leachate was found by McLellan and Rock [35], due to the complexity of the leachates. Peat was not found to be capable of removing metals to acceptable levels for direct discharge, but was sufficient for a pre-treatment (or polishing) process.

5.3. The laundry wastewater

In the laundry wastewater the metal ions formed carbonate and hydroxide complexes according to the calculation (Table 4) or bound to the organic fraction in

the wastewater. Despite this, a rather high metal removal was achieved in the batch experiment. It was observed that the wastewater contained suspended particles. The reason for the high metal removal is probably that the metals were bound to these particles and withdrawn during the filtration operation.

5.4. Metal removal and wastewater composition

The wastewater composition was of great importance for metal removal efficiency, mainly due to the metal speciation. A high degree of metal removal was reached in the sulphide mine leachate, containing mainly free metal ions. A rather high metal removal rate was also reached in the laundry wastewater. The metal ions were probably removed bound to particles withdrawn from the wastewater. The lowest metal removal, and a release of metals initially bound to the adsorbents, occurred in the landfill leachate. A high ionic strength and the

Fig. 4. Removal (%) of Ni, Cu, Zn, Cd, Fe and Ca in the landfill leachate in column experiments. (a) *Sphagnum Cuspidata* peat, (b) *Carex* peat.

metals forming carbonate and organic complexes could explain the result achieved. Generally, the combination of glauconite or clinoptilolite with the peat samples gave a minor improvement in metal removal in column experiments. The total amount of cations adsorbed in column experiments with landfill leachate agreed rather well with the maximum adsorption determined in previous studies. The previously recorded higher increase of metal adsorption onto *Carex* peat than onto *Sphagnum* peat with increased pH values to a high extent explained the slightly higher adsorption of heavy metals onto *Carex* peat than onto *Sphagnum* peat. A higher affinity for Zn adsorption onto *Carex* peat than onto *Sphagnum* peat was indicated. The *Sphagnum* peat sample adsorbed a higher amount of Ca. The differences between the peat types has been attributed to the fact that *Carex* peat has higher S, N and P content, while *Sphagnum* peat has a higher uronic acid content.

6. Conclusion

The wastewater composition was of great importance for metal removal efficiency, mainly explained by the calculated metal speciation.

A high metal removal was achieved in the sulphide mine leachate, where the metal ions to a large extent occurred as free ions. The peat samples decreased the

pH in the leachate, *Sphagnum* peat to a higher extent than *Carex* peat. A higher metal removal was reached with *Carex* peat.

The heavy metal ions in the landfill leachate were to a large extent complex-bound due to a high pH, carbonate and TOC concentration. A low metal removal was achieved. The leachate, high in ionic strength, also seems to have dissolved metal initially bound to the adsorbents.

A high metal removal was reached in the laundry wastewater, which was high in pH and TOC concentration. The metals were probably bound to suspended particles and withdrawn during the filtration operation.

A rather high metal removal from wastewater was generally found using peat as the adsorbent compared to the inorganic adsorbents investigated. Only minor improvement, or no improvement, was observed when peat was combined with clinoptilolite or glauconite in column experiments.

Acknowledgements

Valuable comments from Lars Lövgren on the calculation of metal species in the wastewater are gratefully acknowledged. Financial support was provided by the Swedish Waste Research Council and the Swedish University of Agricultural Sciences.

References

- [1] Cameron RD. Treatment of a complex landfill leachate with peat. *Can J Civ Eng* 1978;5:83–7.
- [2] Coupal B, Lalancette JM. The treatment of waste waters with peat moss. *Water Res* 1976;10:1071–6.
- [3] Lidkea TR. Treatment of sanitary landfill leachate with peat. Vancouver, Canada: The University of British Columbia, 1974.
- [4] Rock CA, Fiola JW, Greer TF, Woodward FE. Potential of *Sphagnum* peat to remove metals from landfill leachate. *J N Engl Water Pollut Control Assoc* 1985;19:32–47.
- [5] Lapakko K, Eger P. Trace metal removal from stockpile drainage by peat. *Inf Circle—US Bur Mines* 1988;1: 291–300.
- [6] Lyons HJ, Reidy TJ. The use of peat in treating landfill leachate. In: Hayes MHB, Wilson WS, editors. *Humic Substances in Soils, Peats and Waters: Health and Environmental Aspects*. Cambridge: Royal Society of Chemistry, 1997. p. 475.
- [7] McLellan J, Rock CA. The application of peat in environmental pollution control; a review. *Int Peat J* 1986;1:1–14.
- [8] Fattahpour Sedeh I, Igsell P, Ringqvist L, Lindström EB. Comparison of metal adsorption properties and determination of metal adsorption capacities of different peat samples. *Resource Environ Biotechnol* 1996;1:111–28.

- [9] Bergner K, Ringqvist L, Igsell P. Charge density in peat and peat particle size fractions and its relation to the botanical origin and degree of decomposition. In: Ringqvist L. Peat as metal trap for wastewater. Acta Universitatis Agriculturae Sueciae, Agraria 226. Doctoral thesis, Swedish University of Agricultural Science, Umeå 2000.
- [10] Ringqvist L, Öborn I. Copper and zinc adsorption onto poorly humified *Sphagnum* and *Carex* peat. Water Res 2002; in press.
- [11] Wu L, Sun Z, Forsling W. Characterization and investigation on the sorption behaviors of SSAB fine dust. Luleå: Luleå University of Technology, 1996.
- [12] Papadopoulos A, Kapetanios EG, Loizidou M. Studies on the use of clinoptilolite for ammonia removal from leachates. J Environ Sci Health, Part A 1996;31:211–20.
- [13] Loizidou M, Haralambous KJ, Loukatos A. Natural zeolites and their ion-exchange behavior towards chromium. J Environ Sci Health, Part A 1992;A27:1759–69.
- [14] Papachristou P, Haralambous KJ, Loizidou M, Spyrellis N. Studies on the nickel removal from aqueous solutions. J Environ Sci Health, Part A 1993;A28:135–42.
- [15] Smith EH, Lu W, Vengris T, Binkiene R. Sorption of heavy metals by Lithuanian glauconite. Water Res 1996;30:2883–92.
- [16] Spoljaric N, Crawford WA. Removal of contaminants from landfill leachates by filtration through glauconitic greensand. Environ Geol 1978;2:359–63.
- [17] Bohlin E, Hämäläinen M, Sundén T. Botanical and chemical characterization of peat using multivariate methods. Soil Sci 1989;147:252–63.
- [18] Bohlin E. Botanical composition of peat. Implications on chemical, microbiological and physical properties. Dissertation, Department of Forest Ecology, Swedish University of Agricultural Sciences, 1993.
- [19] Clymo RS. Ion exchange in *Sphagnum* and its relation to bog ecology. Ann Bot 1963;27:309–24.
- [20] Spearing AM. Cation-exchange capacity and galacturonic acid content of several species of *Sphagnum* in Sandy Ridge Bog, Central New York State. Bryologist 1972;75:154–8.
- [21] Aho M, Tummavuori J. The ion exchange properties of peat Part V: ion exchange properties of some *Sphagnum* peats. Suo 1984;35:67–73.
- [22] Bohlin E, Hämäläinen M. Multivariate evaluation of the significance of quantitative botanical analysis in peat characterization. Anonymous Proceedings of the VIII International Peat Congress. International Peat Society, Leningrad, 1988. p. 211.
- [23] Stumm W, Morgan JJ. Aquatic chemistry: chemical equilibria and rates in natural waters, 3rd ed. New York: Wiley, 1987.
- [24] Öhlander B, Ljungberg J. Acid mine drainage at the Laver Mine, Southern Norrbotten. In: Lövgren L, editor. Workshop on Retention and Mobilization of Heavy Metals in Waste Deposits and Soils, October 18–20, 1994. Swedish Waste Research Council, Stockholm, 1995. p. 22.
- [25] Banks D, Younger PL, Arnesen R-T, Iversen ER, Banks SB. Mine-water chemistry: the good, the bad and the ugly. Environ Geol 1997;32:157–74.
- [26] Herbert Jr RB. Metal transport in groundwater contaminated by acid mine drainage. Nordic Hydrol 1994;25: 193–212.
- [27] Tipping E. WHAM—a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Comput Geosci 1994;20:973–1023.
- [28] Öman C. Emissions of organic compounds from landfills Diss. Department of civil and environmental engineering. Stockholm: Royal Institute of Technology, 1998.
- [29] Eriksson G. An algorithm for the computation of aqueous multi-component, multiphase equilibria. Anal Chim Acta 1979;112:375–83.
- [30] Pettersson C, Håkansson K, Karlsson S, Allard B. Metal speciation in a humic surface water system polluted by acidic leachates from a mine deposit in Sweden. Water Res 1993;27:863–71.
- [31] Stevenson FJ. Umus chemistry: genesis, composition, reactions, 2nd ed. New York: Wiley, 1994.
- [32] Wolf A, Bunzl K, Diesl F. The effect of Ca^{2+} -ions on the adsorption of Pb^{2+} , Cu^{2+} , and Zn^{2+} by humic substances. Chemosphere 1977;5:207–13.
- [33] Zhipei Z, Junlu Y, Zenghui W, Piya C. A preliminary study of the removal of Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Cr^{6+} from wastewater with several Chinese peats. 7th International Peat Congress, vol. 3, Dublin, Ireland, June 18–23, 1984. p. 147–52.
- [34] Aho M. The ion exchange and adsorption of *Sphagnum* peat under acid conditions. Dissertation, Department of Chemistry, University of Jyväskylä, Jyväskylä, 1986.
- [35] McLellan JK, Rock CA. Pretreating landfill leachate with peat to remove metals. Water Air Soil Pollut 1988;37: 203–15.