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TECHNICAL ARTICLE

The Effectiveness of Metal and Metalloid Sorption from Mining Influenced Waters by Natural and Modified Peat

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Abstract

This study investigated the sorption behaviour of natural (N peat) and HCl-acid-modified peat (HCl peat) for contaminants in water collected at a mine site in northern Finland. Batch sorption experiments were conducted at room temperature and at 5 °C. Characterization of the sorbents by FTIR and XPS revealed no substantial change in the peat's functional groups due to the acid treatment. Generally, the N peat was a more efficient sorbent for the mine water, although the HCl peat exhibited better nickel uptake capacity (21 mg Ni/g) than the N peat (16 mg Ni/g) from synthetic water. This is attributed to the lower equilibrium pH in samples treated with the HCl peat as well as the water's different chemical composition. At room temperature, the N peat removed As(V) (80%) and Ni (85%) at low dosage (1–2 g/L), whereas the HCl peat presented good removal of As(V) (80%) at low dosage (1 g/L) but did not achieve satisfactory removal of Ni, even at a higher dosage (4 g/L). The performance of both sorbents was significantly affected by contact time. Ni removal by N peat increased substantially with contact time whereas removals achieved by HCl peat increased slightly up to 60 min, but decreased significantly at 24 h. Unlike with HCl peat, the N peat was less efficient in the experiments conducted at 5 °C. Overall, for both sorbents, As(V) and Ni were the most efficiently removed contaminants from the mine water. HCl peat had slightly better settling properties, however, both products settled poorly, thus rendering the studied mixing and settling system unsuitable for the proposed application. Nevertheless, both peat products, and especially the N peat, exhibited high contaminant removal potential and could represent a cost-effective and sustainable option for mine water treatment.

Keywords Biosorbent · Acid-treated peat · Dosage · Contact time · Arsenic · Nickel

Introduction

Untreated mine water may contain potentially hazardous levels of metals such as lead, copper, nickel, zinc, chromium, cadmium, mercury as well as metalloids such as arsenic and antimony. These elements do not biodegrade and tend to bioaccumulate (Fu and Wang 2011). Conventional water purification methods (e.g. precipitation, adsorption by activated carbon, reverse osmosis, ion exchange), are typically expensive, consume high amounts of energy, and produce additional waste, and so, cannot be considered sustainable (Araújo et al. 2013; Barakat 2011; Eger et al. 2015; Fu and Wang 2011). One of the most promising alternatives is the use of biosorbents such as peat (Brown et al. 2000), sawdust (Yang et al. 2010), rice husk (Sobhanardakani et al. 2013) and corn stalk (Zheng et al. 2012) for removing metals from mining-affected water. These sorbents are abundantly available, cheap, efficient in terms of their sorbent properties, and eco-friendly.

The contaminant removal efficiency of peat, which is a plentifully available biomass in Finland and in countries such as Ireland, Sweden, Germany, Norway, Belarus, and Canada, was evaluated in this study. Peat is a biomass material that naturally forms from the decomposition of vegetation in wet, marshy areas (Brown et al. 2000). Being a humic substance, it is composed of several organic compounds and contains active functional groups such as hydroxyl, carboxyl, sulphonic, and phenolic groups (Bogush et al. 2016), which act as binding sites for metal ions through sorption (Bulgariu et al. 2012). Natural peat has been found to have a high metal uptake capacity (Bartczak et al. 2015; Bulgariu et al. 2011). Several

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methods have been previously investigated to study whether chemical modification could enhance the contaminant uptake capacity of peat. For example, Bulgariu et al. (2011) reported that alkaline treatment of peat using NaOH yielded high metal removal efficiencies, while Gosset et al. (1986) studied metal cation removal by acidified and unacidified peat and reported lower Cu removal by the sieved, acidified peat. But it should be noted that HCl treatment of peat also leads to desorption of metals originally present in its natural form (Gosset et al. 1986). Batista et al. (2009) compared the effect of HCl and HCl + NaOH modification on peat samples taken from different regions and concluded that metal removal by modified peat is highly dependent on the organic matter and mineral content of the different peat samples, and to the modifications. It was also reported that HCl modification does not oxidize the organic content of the peat, thus keeping its organic content intact (Batista et al. 2009).

Although a considerable amount of research has been reported on the efficiency of both natural and modified peat as biosorbents using synthetic waters, there is very little information available on how these biosorbents behave when introduced to real mine waters (Keränen et al. 2015). As such, the main objective of this research was to study the viability of using natural and modified peat for contaminant removal from mining-influenced waters. The peat modification was carried out using HCl, aiming to enhance the wettability and settling properties of the peat, which is naturally quite hydrophobic and exhibits poor settling characteristics. Additionally, the HCl was expected to desorb the contaminants already attached to the natural peat, thus improving the peat's sorptive capacity (Gosset et al. 1986).

The peat sorbents were tested with a water sample collected from a mine site in northern Finland. The tests were carried out at two temperatures (23 ± 2 and 5 ± 2 °C) and with different contact times. In the Nordic countries, where winter is the dominant season, the temperature mostly remains below 0 °C during the winter. As such, it was crucial to assess whether the biosorbent can still efficiently purify mining waters in such cold conditions. A secondary objective was to evaluate the possibility of applying the biosorbents using a "mix and settle" purification system. A small pilot-scale experiment was carried out and the purification efficiency and the biosorbents' settling properties were assessed. The results of the batch sorption study were presented at the 13th International Mine Water Association Congress (Gogoi et al. 2017).

Materials and Methods

Chemicals and Raw Materials

Peat was obtained, in its natural form, from the Stora Enso Veitsiluoto pulp mill in Kemi, northern Finland, which burns peat for energy. The peat used for energy production is moderately decomposed; this type of peat has a high carbon and nitrogen content and a low oxygen and hydrogen content (Andriesse 1988). The ash content of the peat used was measured (using a Precisa prepASH 129 furnace) to be approximately 10% at both 525 and 900 °C. The received peat was dried at 80 °C for 24 h and then sieved to a 90–250 µm size fraction, with the intent of maintaining as similar a size fraction as possible throughout the experiments. Smaller peat particles would have presented settling issues while larger peat particles would have affected the modification experiments, where the larger size would have made it more difficult to wet the peat particles in the acidic solution.

The pre-treated (neutralization) drainage water from the open pit and underground mining area is transferred through ditches to a receiving pond from where it travels to a peatland-based treatment wetland for a polishing treatment phase. Water for the experiments was collected at the receiving pond. The water sample was filtered using a 0.45-µm syringe filter. Stock solutions of HCl (0.2 M) and nickel nitrate [$Ni(NO_3)_2$, 1000 Ni mg/L] were created via dilution in ultrapure Milli-Q water. The pH of the $Ni(NO_3)_2$ solutions was adjusted using 0.1 M HCl or 0.1 M NaOH. Nitric acid (0.5%; HNO_3, 65%) was used to preserve the water samples for elemental analysis.

HCl Modification of Peat

Dried and sieved natural peat (15 g) was weighed in a glass beaker into which 250 mL of 0.2 M HCl was added. The mixture was stirred at 25 °C for 2 h and washed with about 1 L of deionized water to bring the pH to 5 and remove the excess acid. The HCl peat was dried at 60 °C overnight. The same procedure was performed for a second batch using 60 g of peat and 1 L of HCl. The HCl peat gave a yield of 92.1 ± 6.5%.

Batch Sorption Experiments

A pre-selected sorbent mass was weighed and placed in polypropylene bottles into which specific volumes of water were added; they were then transferred to a rotary shaking device (30 rpm/min). The samples were shaken for a predetermined period at room temperature (23 ± 2 °C). Sorbent separation from solution was performed using centrifugation (4500 rpm for 1.5 min), followed by syringe filtration with a 0.45 µm membrane. The extracted solutions were sent for elemental analysis and their final pH was measured. The metal and metalloid removal (%) was calculated using their initial concentration of the unfiltered raw water samples and the residual concentration of the filtered treated water samples. The maximum sorption capacity curve of the sorbents was obtained using a similar batch sorption procedure where 1 g/L of peat sorbent was shaken with 50 mL of the nickel nitrate solutions at Ni concentrations of 2–75.8 mg/L (three replicates). The initial pH of the nickel nitrate solutions ranged between 5.6 and 6.0 and the pH of the mixture was adjusted to 5.8–6.0 after an hour of shaking to avoid a significant pH change. The maximum sorption capacity was calculated as the average value from the top values of the curve (Fig. 2). While studying the effect of sorbent dosage, batch tests were conducted at room temperature (23 ± 2 °C) using 1–4 g/L of peat (two replicates), 200 mL of mining drainage water ($\mathrm{pH_{initial}}$ 7.6–8.0) and 24 h contact time. The effect of the contact time was studied at two temperatures (23 ± 2 °C and 5 ± 2 °C) using a dosage of 2 g/L (two replicates) and contact times of 15, 30, 60 min and 24 h.

Mixing and Settling

The purification efficiency of the mixing and settling system was evaluated for 2 g/L dosage (two replicates) of both natural and HCl-modified peat using a 1 L jar Flocculator 2000 (Kemira Kemwater) equipped with a programmable stirring paddle. A retention time of 60 min was used, with a mixing intensity of 40 rpm and 30 min of settling time. Metal and metalloid removal (%) was calculated using their respective initial concentration of the unfiltered raw water samples and the residual concentration in the filtered treated water samples. An extra replicate of the experiment was conducted in which samples were collected during settling (8 cm from the bottom of the jars, i.e. 10 cm from the water surface) at pre-selected time intervals (0, 1, 2, 3, 4, 6, 8, 11, 13, 17, and 25 min) and measured for turbidity. A settling time of < 30 min was selected to compare the settling behaviour of the natural and modified peat. To evaluate the optimum time required for settling of the peat particles in a real system, a larger-scale experiment would be needed to reduce the scaling-up effect.

Analyses

Elemental analysis of the raw and filtered drainage water was performed using inductively coupled plasma mass spectrometry (ICP-MS), according to standardized method SFS-EN ISO 17294-2:2005. The pH measurements were conducted with a Metrohm 744 pH meter. The electrical conductivity (EC) was measured using a VWR Phenomenal PC 5000H and turbidity was determined with a Hach ratio/XR turbidimeter.

Part of the fresh and treated sorbents were ground into powder using a hand mortar to prepare them for FTIR and XPS analysis. The FTIR spectra of the fresh and treated ground sorbents were measured in the 400–4000 $\mathrm{cm^{-1}}$ wave number region with a Bruker Vertex V80 vacuum FTIR spectrometer and the OPUS program. The XPS spectra were carried out for fresh (as such and ground) and treated (ground, 2 g/L, room temperature, 24 h, washed with deionized water until neutral pH was attained) sorbents with a Thermo Fisher Scientific ESCALAB 250Xi using a monochromatic Al Kα source (1486.6 eV). The sorbents were mounted on indium foil. The XPS data were analysed with Advantage software, and the Shirley function was used to subtract the background. The charge correction was performed by setting the binding energy of the adventitious carbon to 284.8 eV. The C 1 s spectra were fitted using a Shirley background and a Gaussian–Lorentzian sum function.

Results

Characterization of Drainage Water

The characteristics of the mine water (raw and filtered) are listed in Table 1. The raw mine water had an EC of 2.3 mS/cm, and a pH of 7.7. Although the drainage water contained a wide range of trace elements, this study focused on As(V), Ni, Mn, and Sb(V). Ni and Mn were considered to be present as cations (Bartczak et al. 2015; Nádáská et al. 2012) and As(V) and Sb(V) in anionic form. Nicomel et al. (2015) state that As is present as As(V) under aerobic oxidizing conditions such as surface waters, whereas Polack et al. (2009) report Sb(V) to be the dominant form of Sb in oxic water systems. As(V) exists as $\mathrm{HAsO_4^{2-}}$ at pH 7–12 (Ansone-Bertina and Klavins 2016) and Sb(V) as $\mathrm{Sb(OH)_6^-}$ in mildly acidic to alkaline solutions (Filella et al. 2002).

Characterization of Biosorbents

The FTIR spectra of N peat and HCl peat are presented in Fig. 1a, which shows that both sorbents exhibited similar peaks, indicating no visible changes due to acid treatment. Broad bands at 3421 and 3529 $\mathrm{cm^{-1}}$ were observed in both peat materials, representing the presence of hydroxyl groups and hydrogen bonds, as it has been well established that the spectral range between 3200 and 3600 $\mathrm{cm^{-1}}$ represents these functional groups (Nakanishi 1962; Williams and Fleming 1995). Groups of methoxyl and $\mathrm{–OCH_3}$ (C–H stretching vibrations) can be seen at transmittance bands 2920 and 2921 $\mathrm{cm^{-1}}$ (Hergert 1960). Stretching vibrations of C–H have also been observed at 2852 $\mathrm{cm^{-1}}$ (Bartczak et al. 2015). In both the N peat and HCl peat, carboxylic groups (COO–) were present at 1650 $\mathrm{cm^{-1}}$, whose presence is supported by Bulgariu et al. (2011), where the FTIR spectral range between 1600 and 1650 $\mathrm{cm^{-1}}$ of natural and modified peat proved to be related to carbonyl bonds from carboxylic acids. The stretching vibrations of C–O bonds were exhibited at 1091 $\mathrm{cm^{-1}}$, which according to Bartczak et al. (2015) appear

Table 1 Mining drainage water quality characteristics

	Mining drainage water (raw)	Mining drainage water (filtered)
Kok. N (µg/L)	14,000	15,000
NO_3–N (µg/L)	7800	8100
NO_2–N (µg/L)	340	330
NH_4–N (µg/L)	5500	5600
Cl^- (mg/L)	84	85
SO_4^{2-} (mg/L)	1000	1000
DOC (mg/L)	3.9	3.4
Conductivity (mS/cm)	2.3	
Al (µg/l)	79.4	11.7
As (µg/L)	28.6	16.9
Fe (µg/L)	591	12.9
Mn (µg/L)	1510	1440
Ni (µg/L)	128	134
Sb (µg/L)	180	158
B (µg/L)		92.2
Ba (µg/L)		49.9
Be (µg/L)		< 0.05
Cd (µg/L)		0.09
Co (µg/L)		12.6
Cr(µg/L)		0.23
Cu (µg/L)		0.93
Hg (µg/L)		< 0.1
Mo (µg/L)		14.2
Pb (µg/L)		0.12
Se (µg/L)		0.54
Sn (µg/L)		< 0.05
Sr (µg/L)		1750
Tl (µg/L)		0.03
U (µg/L)		0.73
V (µg/L)		0.21
Zn(µg/L)		8.2
Ca (mg/L)		355
K (mg/L)		11.2
Mg (mg/L)		101
Na (mg/L)		69.7
P (mg/L)		< 0.05
S (mg/L)		383
Si (mg/L)		6.71

in the range of 110–1000 cm^{-1}. Interestingly, the used N peat and HCl peat had nearly identical spectra (Fig. 1a) to their fresh forms, thus it could be inferred that the sorbents were fairly stable.

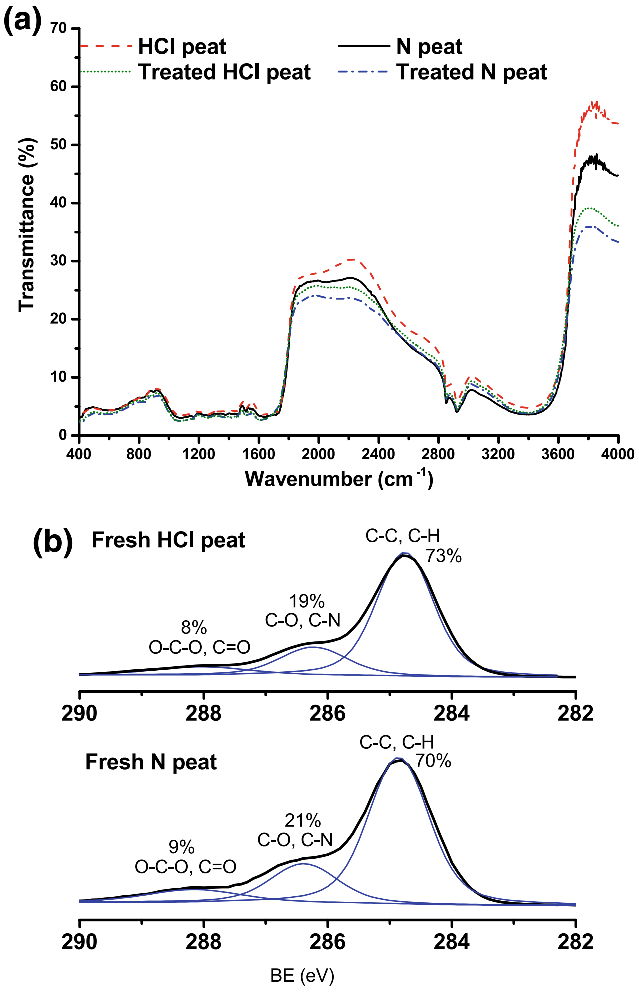

Fig. 1 **a** FTIR spectra of fresh and treated N peat and HCl peat samples; **b** XPS spectra of C 1 s for fresh HCl-treated and natural peat (measured as such). Thick solid line: experimental curve; thin solid line (blue): fitting curve

According to the XPS data, the fresh N peat and HCl peat surface (measured as such) contained mainly carbon (78.7 and 80.7% atm., respectively) and oxygen (18.5 and 17.0% atm.) with small amounts of nitrogen (2.5 and 2.0% atm.), sulphur (0.19% atm., both) and iron (0.1 and 0.05% atm.). Due to the low content of other elements, such as iron, it can be inferred that the biomaterial itself was mainly responsible for the metal and metalloid removal. The C 1 s spectra of fresh peat products (measured as such) were fitted to three peaks (Fig. 1 b), namely (1) aromatic and aliphatic carbon (C–C, C–H; 284.8–284.9 eV), (2) carbon having a single bond with oxygen and nitrogen (C–O, C–N; 286.2–286.4 eV) and (3) carbon having two bonds with oxygen (O–C–O, C=O; 288.0–288.2 eV). HCl treatment of peat did not significantly affect the element content of the peat surface or the C 1 s spectrum. The N 1 s spectrum showed a single peak at 400.0–401.0 eV and the nitrogen in N peat was mainly present in amide form. The presence of small amounts of pyridinic nitrogen peaks and quaternary nitrogen is possible with peat material, and

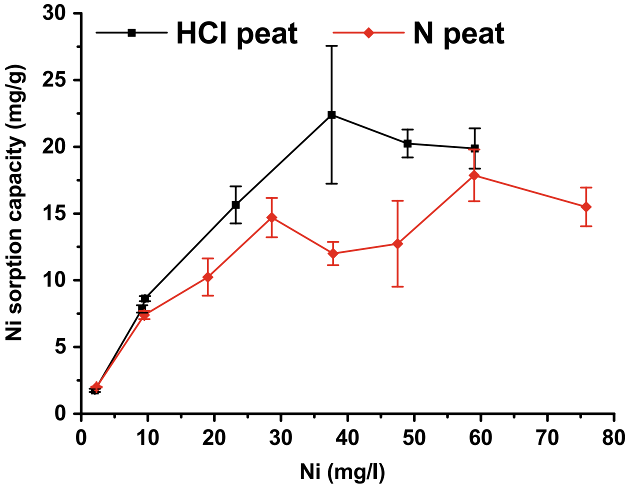

Fig. 2 Nickel sorption capacity of N peat and HCl peat. Dosage 1 g/L, contact time 24 h, temperature 23 ± 3 °C. Error bars represent variation between the three experimental replicates

they exist at the lower and higher binding energy (BE) sides of the amide nitrogen peak (Kelemen et al. 2006).

Maximum Capacity

Maximum Ni sorption capacity curves for natural and modified peat are presented in Fig. 2. HCl peat exhibited around 25% higher Ni sorption capacity than N peat. The maximum Ni sorption capacity determined for N peat was approximately 16 mg Ni/g while for HCl peat, it was approximately 21 mg Ni/g. Generally, the determined maximum sorption capacity for N peat was significantly higher than that found in the literature. For example, Ho et al. (1995) reported 9.18 mg Ni/g as the maximum Ni uptake capacity by natural peat.

Effect of Sorbent Dosage

Metal and metalloid removal efficiencies were evaluated (dosages 1–4 g/L, 23 ± 2 °C and 24 h contact time) for Al, As(V), Fe, Mn, Ni, and Sb(V). However, most of the Al and Fe contained in the mine water was removed during filtration (Table 1). Hence, the removal rates of As(V), Mn, Ni, and Sb(V) by the biosorbents were calculated (Fig. 3). The pH of the treated water decreased with increasing sorbent dosages. This pH decrease was more accentuated in the HCl peat treated samples ($pH_{24h} = 4.6–6.6$) than in the N peat samples ($pH_{24h} = 6.1–7.1$).

N peat proved to be a highly efficient sorbent, achieving > 80% Ni removal and > 70% As(V) removal at all tested dosages (Fig. 3a). The optimum peat dosage identified for Ni removal was 2 g/L, whereas for As(V), 1 g/L was optimal. Low removal efficiencies were observed for Mn and Sb(V) at all tested dosages. The overall sorption of the HCl peat was significantly less than that of the N peat (Fig. 3b). Efficient As(V) removal (80%) at 1 g/L was achieved by HCl peat; however, higher dosages exhibited lower to negligible removal results. Even at the highest dosage (4 g/L), the HCl peat could only remove about 30% Ni. In contrast to removal with N peat, Sb(V) removal increased with increasing dosages of HCl peat, reaching 50% removal at 4 g/L.

Only slight changes were noticed between the surface composition of the fresh and used sorbents. For instance, more iron (≈ 0.16 atomic %) and a small amount of calcium (≈ 0.5 atomic %) were observed on the sorbent surfaces. XPS detected no As(V), Mn, Ni, or Sb(V).

Effect of Contact Time and Temperature

The effect of contact time on the sorption efficiency of N peat and HCl peat was tested at room temperature (23 ± 2 °C) and at 5 °C (Figs. 3, 4). It was observed that beyond the optimal contact times, the pollutant removal efficiency either decreased or remained stable, at higher contact times. Leaching of Mn into the treated samples occurred, so Mn removal is not reported in the figures. Mine water samples treated with HCl peat exhibited a more significant drop in pH ($pH_{24h} = 5.8$) than with N peat ($pH_{24h} = 6.6$).

As(V) and Ni were the only components effectively removed in the experiments with N peat conducted at 23 ± 2 °C (Fig. 3a). Their removal rates increased linearly with contact time. Optimum Ni removal (85%) was achieved after 24 h. For As(V), the optimum contact time was 60 min, resulting in 70% removal, although a slight increase was observed with additional contact time. In the case of HCl peat (Fig. 3b), the optimum contact time was 30 min for As(V) and Ni (50 and 55% removal, respectively). Overall, the sorption efficiency of the HCl peat was less than that of N peat, irrespective of contact times, and removal (%) decreased with more contact time.

The effect of contact time at low temperature (5 ± 2 °C) is shown in Fig. 4. The pH_{24h} of mine water samples treated with HCl peat and N peat was around 6.2 and 6.8, respectively. Sorption was less efficient at 5 °C than at room temperature with N peat. However, for the same sorbent, As(V) and Ni removal (%) increased with time; the optimum As(V) (60%) and Ni (50%) removal was achieved at 60 min. However, no significant dependence on contact time was observed for the HCl peat, although there was a slight increase in the amount of As(V) removal at 60 min (55%) compared to 30 min of contact time (50%).

Mixing and Settling System

In a mixing and settling water purification system, the sorbent is added to the water and mixed for the required contact

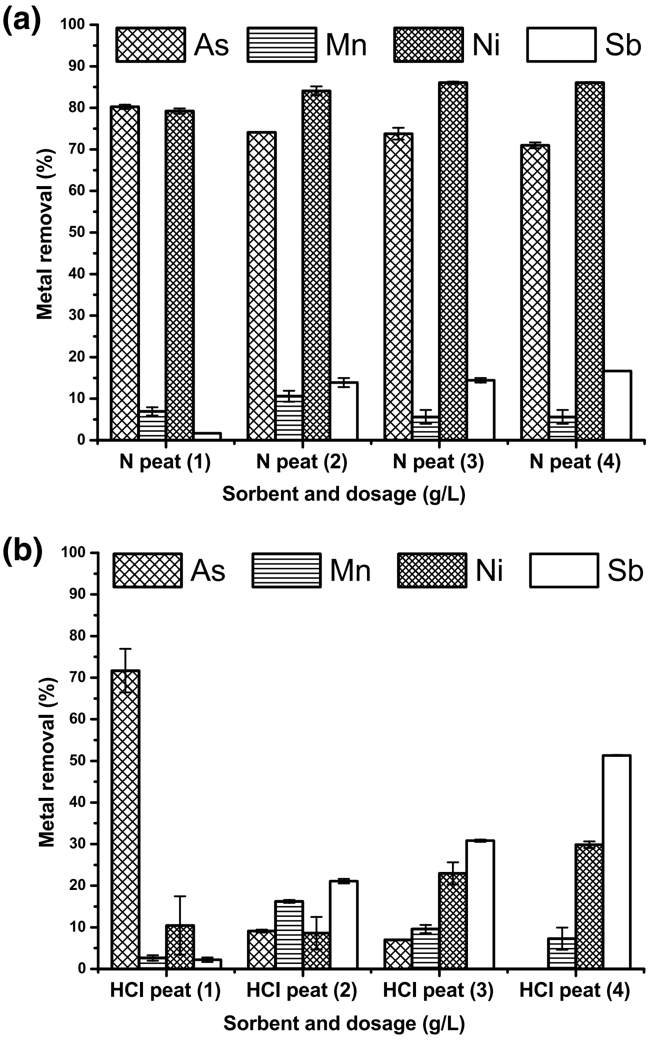

Fig. 3 Effect of sorbent dosage (1, 2, 3 and 4 g/L) on metal removal % using **a** N peat and **b** HCl peat. Initial metal concentrations: As 28.6 µg/L, Ni 128 µg/L, Mn 1510 µg/L and Sb 180 µg/L. 23 ± 2 °C. Error bars represent max and min of experimental replicates

time. The suspension is then transferred to a settling tank or basin where the sorbent settles out of the suspension, accumulating at the bottom, as the purified water overflows and is discharged. Retention time in the system and the dosage of sorbent are important because they directly affect costs. Therefore, a 60 min contact time and an optimum dosage of 2 g/L of both sorbents were selected based on the batch experiment results.

Removal of Mn and Sb(V) was low for both sorbents but slightly higher removals were achieved by the HCl peat. Generally, removal efficiencies were very similar to those obtained at 60 min of contact time during the batch experiments (Fig. 5). Overall, the N peat performed slightly better than the HCl peat (Fig. 6a). While N peat removed around 65% As(V) and 60% Ni, HCl peat achieved just over 50% removal of As(V) and Ni.

An important aspect of applying sorbents in a mixing/settling system is the settling properties of the sorbent particles. The settling properties of the used sorbents were evaluated by monitoring the removal of turbidity over time during the sedimentation stage of treatment. The addition of both peat sorbents increased the turbidity significantly (Fig. 6b), with the HCl peat causing greater turbidity. Although turbidity decreased with time, the values after 25 min (HCl peat, 25 NTU and N peat, 47 NTU) still significantly exceeded the initial turbidity of the water (6.5 NTU). Furthermore, significant flotation of particles of both sorbents was observed. As the water was extracted from below the surface, these floating particles adhered to the sides of the glass beaker and were therefore not included in the sample.

Discussion

Both the natural and modified forms of peat contained typical functional groups, such as carboxylic acid and phenolic hydroxide groups. These functional groups given out by humic acid complexes react with metals to release protons (Brown et al. 2000; Crist et al. 1996). The metal uptake nature of peat is based on the hydrolytic adsorption

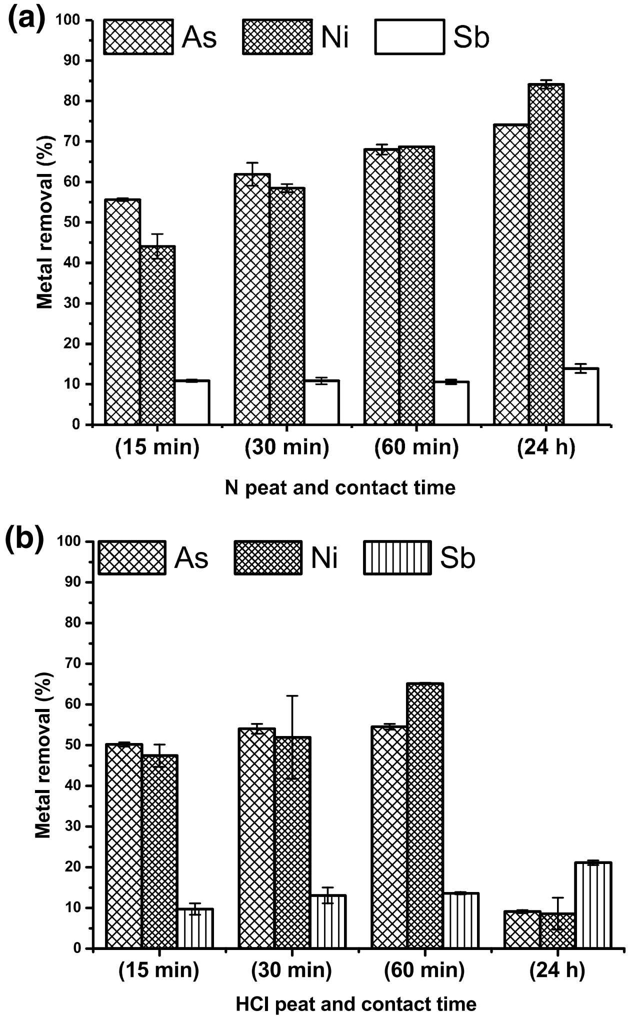

Fig. 4 Effect of contact time (23 ± 2 °C, 2 g/L dosage) on metal removal (%) from mining wastewater using **a** N peat and **b** HCl peat. Initial metal concentrations: As 28.6 µg/L, Ni 128 µg/L, Mn 1510 µg/L and Sb 180 µg/L. Error bars represent max and min of experimental replicates

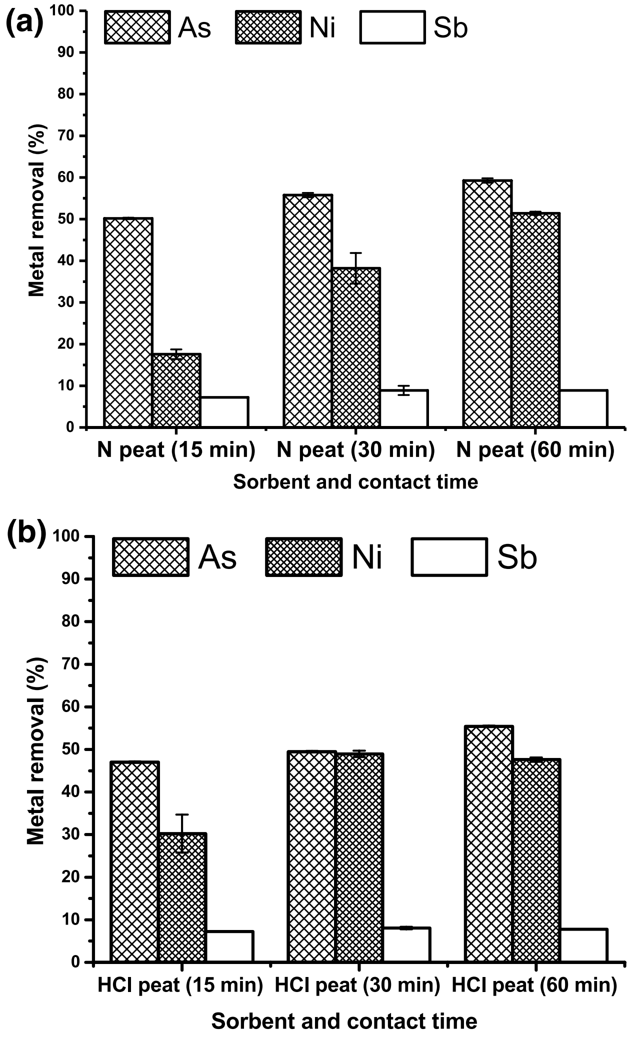

Fig. 5 Effect of time (5 ± 2 °C, 2 g/L) on metal removal (%) from mining wastewater using **a** N peat and **b** HCl peat. Initial metal concentrations: As 28.6 µg/L, Ni 128 µg/L, Mn 1510 µg/L and Sb 180 µg/L. Error bars represent max and min of experimental replicates

of positively charged metal ions by the negatively charged functional groups (Ong and Swanson 1966). Nevertheless, the sorption efficiency of a sorbent for a particular contaminant in solution depends on several factors, such as the type and concentrations of ions in water, water pH and temperature, contact time, and ion affinity to the active site.

Among the factors influencing metal or metalloid sorption by peat, pH is especially important. While the experiments with synthetic water were conducted at controlled pH values of 5.8–6, the pH of the mine water was not adjusted throughout the sorption experiments. The goal was to test the efficiency of the sorbents in a real application where pH adjustment is not a practical option due to the large volumes of drainage water to be treated. Bartczak et al. (2015) reported that pH values of 5–6 would be the optimum range for Ni sorption. At too acidic a pH (1–3), hydrogen ions compete with metal ions for sorption onto the sorbent's surface, and at an alkaline pH (> 7.5), Ni is precipitated as hydroxide. Thus, in order to avoid Ni precipitation and at the same time achieve optimum Ni removal through sorption, the tests with synthetic water were run at pH 5.8–6. Higher pH levels can cause increased dissociation of peat's functional groups, which in turn increases electrostatic interaction with metal cations (Bulgariu et al. 2012).

During this study, the acid treatment of the peat contributed to the lower equilibrium pH of the treated water, presumably due to the release of hydrogen ions. The released hydrogen ions in turn compete with the dissolved metal cations for attachment to the functional groups on the peat surface. This may explain the poorer overall sorption

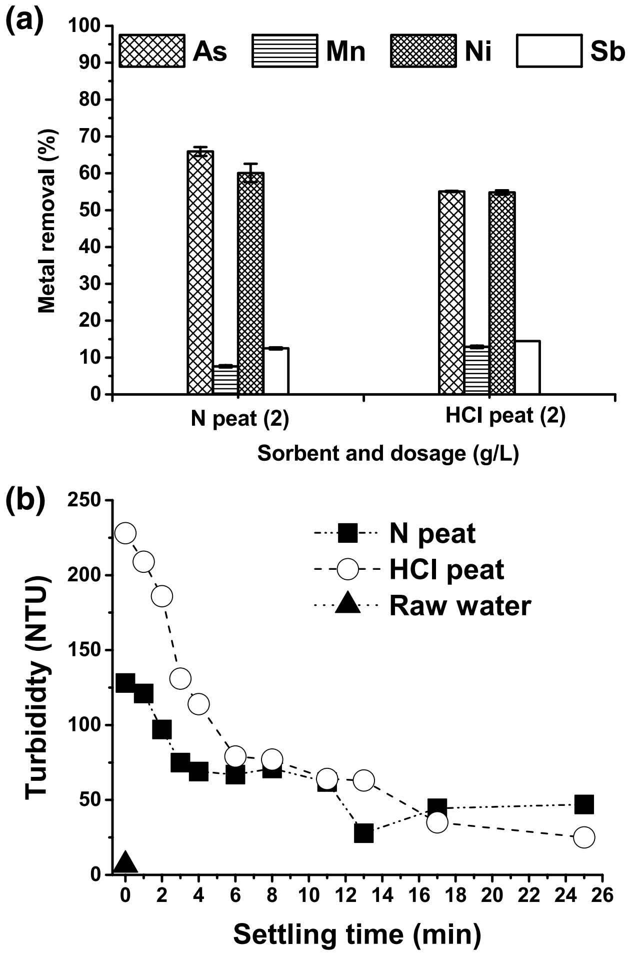

Fig. 6 **a** Metal removal (%) using N peat and HCl peat when tested using mixing and settling system. Initial metal concentrations: As 28.6 µg/L, Ni 128 µg/L, Mn 1510 µg/L and Sb 180 µg/L. Error bars represent max and min of experimental replicates. **b** Settling of N peat and HCl peat as a function of time. 40 rpm mixing speed, 60 min retention time. 23 ± 2 °C

performance by the HCl peat. However, the HCl treatment could have made anionic binding sites more readily available, which might have led to the removal of Sb(V) at high HCl peat dosage. However, the HCl peat did not remove As(V) as efficiently at the same high dosage, highlighting the role of ion affinity towards the peat sorbent. Alternatively, it might indicate that all of the free anionic binding sites on the HCl peat were occupied by Sb(V), thus reducing As(V) removal at the same dosage. Therefore, a straight comparison between the sorbents is difficult due to the different equilibrium pH values of the treated drainage water. Gosset et al. (1986) reported that unsieved and unacidified samples of peat removed copper better than sieved, acid-modified peat samples. However, other studies, such as the one reported by Batista et al. (2009), found that HCl modification of certain peat samples increased their Cr(III) uptake. The organic and mineralogical composition of the peat also plays a role in its sorption efficiency (Batista et al. 2009).

The quality and composition of the drainage water played an important role in the sorptive performance of the peat. The nickel uptake capacity of the HCl peat was substantially better than that of the N peat for synthetic nickel solutions, but the results were the opposite with real mine water. Of course, similar results might not be observed in the treatment of different water samples. In addition, although the mine water contained several elements (Table 1), this study focused only on As(V), Ni, Sb(V), and Mn. The inference is that the sorption performance of natural and modified peat is highly dependent on the type of water being treated. Although peat exhibits high sorption efficiency in laboratory tests with synthetic solutions, its efficiency may differ greatly in real wastewater, due to, for example, to the presence of organic substances that can form complexes with the metals (Bulgariu et al. 2012). The formation of such metal–organic complexes could increase the solubility and bioavailability of the metal ions.

Throughout the experiments, As(V) and Ni were the most efficiently removed ions, followed by Sb(V) and Mn. Kalmykova et al. (2008) inferred that the sorption efficiency of peat was higher for ions with higher electronegativity. The electronegativity (on the Pauling scale) for As(V), Ni, Sb(V), and Mn is 2.18, 1.91, 2.05, and 1.55, respectively, which, supports the higher removal efficiencies of As(V) and Ni by the peat sorbents. However, although Sb(V) had a higher electronegativity than Ni, it was not as efficiently removed by either of the sorbents (except in the case of high HCl peat dosage). This can be attributed to the higher affinity of cations onto the peat, as compared to anions. Ansone-Bertina and Klavins (2016) reported that although As(V) and Sb(V) have similar chemical properties, their sorption efficiency with respect to peat is dependent on structural aspects, such as their molecular size and coordination. As(V) is a tetrahedral oxyanion with a smaller ionic radius and a higher charge density than Sb(V), which is an octrahedral oxyanion (Ansone-Bertina and Klavins 2016).

While evaluating the effect of contact time (23 ± 2 °C), it was observed that once equilibrium was achieved, the sorbents reached saturation and prolonged contact time led to contaminant desorption from the modified peat sorbent. The attainment of equilibrium by peat at an early contact time has also been reported by Bartczak et al. (2015) who found 15–30 min contact time to be optimum for Ni removal. Furthermore, Qin et al. (2006) confirmed that a short contact time was required to achieve equilibrium by peat. Their study showed that optimum removal of Pb, Cu and Cd was achieved with 60 min of sorption time. These studies revealed that, beyond these optimum contact times, the sorption efficiency did not increase. Thus, it is crucial that the mining drainage waters are kept in contact with the sorbent only until the equilibrium contact time is achieved in order to obtain optimum contaminant removal. Regarding the effect of temperature, the lower sorption efficiency by N peat at 5 ± 2 °C revealed that temperature played a key role in the sorption behaviour of N peat, while acid-modified peat was not significantly affected by the change in temperature. It could be that cold temperature conditions necessitate longer contact times than the ones tested in this study for efficient removal of metal and metalloids by peat.

Small-scale pilot experiments regarding the suitability of using peat sorbents in a mixing/settling system showed that although satisfactory pollutant removal efficiency could be achieved (based on filtered samples), the settling characteristics of the peat particles affect the feasibility of the system. As stated by Kløve (1997), the low settling velocity of peat makes its application in water treatment complicated. HCl treatment made the peat less hydrophobic. This was probably due to leaching of some humic substances (Leiviskä et al. 2018) or increased the porosity of the modified sorbent, thereby leading to more steady settling behaviour. However, significant floating of particles was observed with both peat samples. Failure to remove the added sorbent would lead to the discharge of sorbent particles into water bodies, contributing to siltation and water quality deterioration. Furthermore, the sorbed metal species could leach under different conditions, thus being released into the environment. Further research is suggested where modifications to the settling basin could be evaluated as a low-cost solution. For example, floating barriers could be added to accumulate the floating particles, which would subsequently settle as aggregates. However, due to the intrinsic properties of the peat, it appears that a mixing system followed by a filtration stage where complete removal of particles is achieved would be a more viable solution. However, issues such as the cost and energy requirements of the additional filtration system should be carefully evaluated.

Regarding the economic feasibility of using peat as a low-cost sorbent, peat has been reported to be have a better sorption efficiency than that of several more conventional treatment methods (Baileyab et al. 1999). Peat is abundant in Finland and the amount of peat produced is higher than the amount being used. The chemical modification method used in this study to modify the natural peat was very practical, not time-consuming, and required small quantities of chemicals. The modified peat was recovered easily through centrifugation or filtration, depending on the quantity of the batch. The water used to wash the modified peat could be recovered and circulated to wash subsequent batches of modified peat, thus reducing water consumption. The sorptive process was also simple, once the sorbents were applied to specific drainage water solution volume and the mixing speed was set. Overall, the sorbents presented a number of characteristics that made them a beneficial alternative for the treatment of dilute drainage water streams, such as the one used in this study. Another factor crucial for the economic feasibility of peat as a sorbent is the possibility of its recovery and reuse. Periodic replacement of peat is required when treating large volumes of water. The recovered peat can be acid-washed to desorb the contaminants it has retained and then re-applied. FTIR results of the used/recovered peat samples revealed that the used peat contained the same functional groups as its fresh counterpart, indicating that the sorbent material was quite stable. Hence, re-use of recovered peat would not affect its sorption efficiency. A more viable option regarding the reuse of recovered peat would be to use the peat for energy production, which is what most peat is used for in Finland.

Conclusions

Overall, the N peat achieved better sorption efficiency than the HCl-treated peat for the mine drainage water. The equilibrium pH of the HCl peat was considerably less than that of the N peat, which could have led to its lesser sorption efficiency. The sorption efficiency of the N peat was higher at room temperature (23 ± 2 °C) than at cold temperatures (5 ± 2 °C); however, the performance of HCl peat was unaffected by the temperature change. As(V) and Ni were removed more efficiently by both peat products than the Mn and Sb(V), with the exception of some greater Sb(V) removal rates at higher HCl peat dosages. The removal of As(V) was fairly independent of contact time while Ni removal was highly dependent on contact time. Regarding the use of peat sorbents in a mixing/settling purification system, although HCl modification helped the settling characteristics to some extent, the poor settling properties of the tested sorbents might render this approach improbable.

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