Removal of Metals from Mining Wastewaters by Utilization of Natural and Modified Peat as Sorbent Materials

Gogoi, H.[1], Leiviskä, T.[1], Heiderscheidt, E.[2], Postila, H.[2] & Tanskanen, J.[1]

[1] *University of Oulu, Chemical Process Engineering, P.O. Box 4300, FIN-90014, University of Oulu, Oulu, Finland*
[2] *University of Oulu, Water Resources and Environmental Engineering, P.O. Box 4300, FIN-90014, University of Oulu, Oulu, Finland*

Abstract This study investigated metal removal efficiency of natural (N peat) and HCl treated peat (HCl peat) using batch sorption tests with real mining wastewaters. FTIR and XPS studies revealed that peat modification did not alter the structure of the sorbent. HCl peat exhihited higher maximum metal uptake capacity (22.4 mg Ni/ g) than N peat (17.9 mg Ni/g). Sorbents removed arsenic most efficiently (80%, dosage 1 g/L). Optimum contact times ranged between 30-60 min. Our study revealed that although HCl peat had better settling properties, N peat displayed overall better purification performance, representing thus the most cost-effective and sustainable option.

Key words Biosorbent, sorption, dosage, contact time

Introduction

Mining wastewater releases metals such as lead (Pb), copper (Cu), nickel (Ni), zinc (Zn), chromium (Cr), cadmium (Ca), mercury (Hg) and manganese (Mn) into the environment. These metals are hazardous as they do not biodegrade and tend to bioaccumulate (Fu & Wang 2011). In an attempt to provide a sustainable alternative to conventional water purification methods, the application of biosorbents was studied. The metal removal efficiency was assessed of natural and modified peat, a cheap and abundantly available biomass in Finland. Peat consists of organic compounds with various active functional groups such as hydroxyl, carboxyl, sulphonic and phenolic groups, which are responsible for the rapid metal cation uptake onto their surface (Bartczak *et al.* in press).

However, little information is available on how such biosorbents behave when introduced into real wastewaters (Keränen *et al.* 2015). Thus, the main objective of this research was to study the viability of using natural (N peat) and modified peat (HCl peat) for metal removal from wastewaters obtained from a mining site in northern Finland. The modification of peat was performed using hydrochloric acid (HCl), aiming at enhancing the wettability and settling properties of N peat since it is quite hydrophobic and exhibits poor settling behavior. Additionally, HCl treatment should desorb metal ions, which are sorbed on N peat, improving its metal sorption capacity. The goal was to evaluate the sorption efficiency of N peat and HCl peat at different contact times and temperatures (23 °C and 5 °C) to simulate the conditions that can be found in different applications.

Materials and Methods

Chemicals and raw materials

Peat obtained from Stora Enso Veitsiluoto pulp mill in Kemi, Finland was dried at 80 °C for 24 h and sieved to 90-250 µm size fraction. The raw mining drainage water tested had the following characteristics: 79.4 µg/L aluminum (Al), 28.6 µg/L arsenic (As), 591 µg/L iron (Fe), 1510 µg/L Mn, 128 µg/L Ni, 180 µg/L antimony (Sb), 3.9 mg/L dissolved organic carbon (DOC), 14000 µg/L total nitrogen, 7800 µg/L NO_3-N, 340 µg/L NO_2-N, 5500 µg/L NH_4-N, 84 mg/L chlorine, 1000 mg/L SO_4. Filtered samples (0.45 µm) of the mining drainage water contained: 9.15 µg/L Al, 16.2 µg/L As, 9.85 µg/L Fe, 1475 µg/L Mn, 129.5 µg/L Ni, 170 µg/L Sb and 3.4 mg/L DOC. The measured electrical conductivity was 2.3 mS/cm.

The dilution of concentrated HCl solution and dissolution of solid nickel nitrate ($Ni(NO_3)_2$) in ultrapure Milli-Q water were conducted in the creation of stock solutions (HCl 0.2 M and 1000 Ni mg/L). The pH of the $Ni(NO_3)_2$ solutions was adjusted using 0.1 M HCl and 0.1 M NaOH. Nitric acid (0.5%) (HNO_3, 65%) was used in the preservation of water samples for metal analysis.

HCl modification of peat

Raw peat (15 g) was weighed in a glass beaker to which 250 mL of 0.2 M HCl was added. The mixture was stirred at 25 °C for 2 h and washed with water (about 1000 mL was used in total) to bring the pH to 5. The product (HCl peat) was dried at 60 °C overnight. The same procedure was performed for a second batch using 60 g of peat (1L of HCl was used). The HCl peat gave a yield of 92.1± 6.5 %.

Batch Sorption Experiments

Pre-selected sorbent mass was weighed and transferred to polypropylene bottles. A pre-selected volume of water was then added to the bottles, which were then transferred to some rotary shaker equipment (30 rpm/min). The samples were shaken for a pre-determined period at room temperature (23 ± 2 °C) and the sorbents were then separated from solution by centrifugation (4500 rpm for 1.5 min) followed by syringe filtration (0.45 µm). The extracted solutions were sent for metal analysis and their final pH was measured. The maximum sorption capacity curve of the sorbents was obtained using a similar batch sorption procedure where 1 g/L dosage of peat sorbent was shaken with 50 mL of the nickel nitrate solutions (2-75.8 mg/L). The initial pH of the nickel nitrate solutions ranged between 5.6-6.0 and the pH of the mixture was adjusted to 5.8-6.0 after one hour of shaking to avoid a significant pH change. While studying the effect of the dosage, batch tests were conducted at room temperature (23 ± 2 °C) using 1-10 g/L of peat sorbent, 200 mL of mining drainage water ($pH_{initial}$: 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 and contact times of 15 min, 30 min, 60 min and 24 h.

Analyses

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

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

Results

Characterization of Biomass Sorbents

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 cm^{-1} and 3529 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 3200-3600 cm^{-1} represents these functional groups (Nakanishi 1962; Williams and Fleming 1995). Groups of methoxyl and -OCH_3, (C-H stretching vibrations) can be seen at transmittance bands 2920 cm^{-1} and 2921 cm^{-1} (Herbert 1960). Stretching vibrations of C−H have also presented at 2852 cm^{-1} (Bartczak *et al.* in press). In both N peat and HCl peat, carboxylic groups (COO−) were present at 1650 cm^{-1}, which presence is supported by Bulgariu *et al.* (2011), where the FTIR spectral range between 1600-1650 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 cm^{-1}, which according to Bartczak *et al.* (in press) appear in the range of 110-1000 cm^{-1}. Interestingly, the N peat and HCl peat used had nearly identical spectra (Fig. 1a) to their fresh forms, thus it could be inferred that the sorbents were fairly stable.

According to the XPS data, the fresh N peat and HCl peat surface contained mainly carbon and oxygen with small amounts of nitrogen, sulphur and iron. The C 1s spectra of fresh peat products 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 1s spectrum. The N 1s spectrum showed a single peak at 400.0-401.0 eV and the nitrogen in 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 they exist at the lower and higher BE side of the amide nitrogen peak (Kelemen *et al.* 2006).
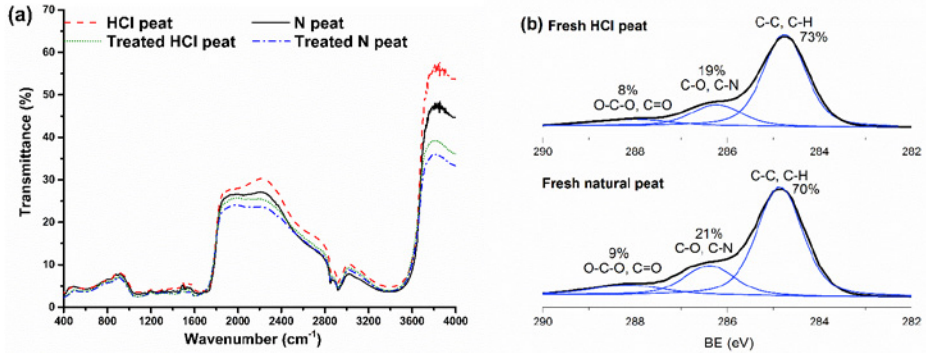
Figure 1. (a) FTIR spectra of fresh and treated N peat and HCl peat samples; (b) XPS spectra of C 1s for fresh HCl-treated and natural peat. Thick solid line: experimental curve; thin solid line (blue): fitting curve.

Maximum Capacity and Effect of Sorbent Dosage

The maximum sorption capacity obtained for N peat was 17.9 mg Ni/g while for HCl peat it was 22.4 mg Ni/g (data not shown). Thus, HCl peat exhibited a higher metal sorption capacity compared to N peat. The metal removal efficiency of the peat sorbents from mining drainage waters at different dosages (1-4 g/L), room temperature and 24 h contact time were evaluated for Al, As, Fe, Mn, Ni and Sb but it was observed that most of the Al and Fe were removed when the mining drainage water was filtered (0.45 μm syringe filters). Hence, removal rates of As, Mn, Ni and Sb were analyzed (Fig. 2). The pH of treated wastewater decreased with an increasing sorbent dosage. The pH decrease was more accentuated in the HCl peat treated samples (pH_{24h} = 4.6-6.6) than in the N peat treated samples (pH_{24h} = 6.1-7.1).
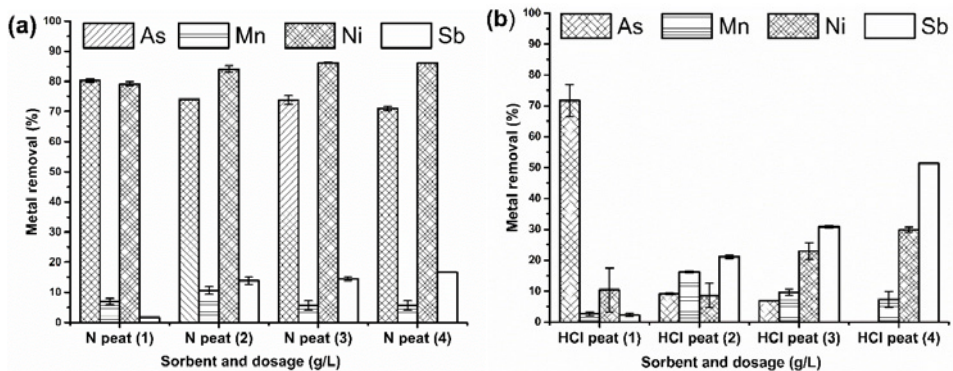
Figure 2. Effect of sorbent dosage (1, 2, 3 or 4 g/L) on metal ion removal % using (a) N peat and (b) HCl peat. 23±2 °C. Error bars represent max and min of experiment replicates.

N peat proved to be a highly efficient sorbent, which achieved >80% Ni removal and >70% As removal at all tested dosages (Fig. 2 a). The optimum dosage for Ni removal was 2 g/L while for As it was 1 g/L. Low removal efficiencies were observed for Mn and Sb at all tested dosages. The sorption performance of HCl peat was significantly lower than that of N peat (Fig. 2 b). Efficient As removal (80%) at 1g/L was achieved; however, higher dosages exhibited lower to negligible removal results. Unlike with N peat, Sb removal increased with an increasing dosage of HCl peat, reaching 50% removal at 4 g/L.

When comparing the surface composition of fresh and used sorbents, only slight changes could be noticed. For instance, a larger amount of iron (≈0.16 atomic %) and the appearance of a small amount of calcium (≈0.5 atomic %) was observed at the sorbents' surfaces. The presence of As, Mn, Ni and Sb was not detected by XPS.

Effect of Contact Time and Temperature

The effect of contact time on the metal removal efficiency of N peat and HCl peat was tested at room temperature (23 ± 2 °C) and at 5 °C (Fig. 3 and 4). Leaching of Mn into the treated wastewaters occurred, thus Mn is not represented in the figures. The wastewater samples treated with HCl peat exhibited a more significant drop in pH (pH_{24h} = 5.8) compared to N peat (pH_{24h} = 6.6).

Regarding the experiments with N peat conducted at 23 ± 2 °C (Fig. 3 a), As and Ni were the only metals effectively removed. Their removal rates increased linearly with contact time. Optimum Ni removal (85%) was achieved after 24 h. For As, the optimum contact time was 60 min resulting in 70% removal, although a slight increase in removal at a higher contact time was observed. In the case of HCl peat (Fig. 3 b), the optimum contact time was 30 min for As and Ni (50% and 55% removal, respectively). Overall, the metal removal efficiency of HCl peat was lower than that of N peat irrespective of the contact times, and the metal being evaluated (%) significantly decreased at 24 h contact time.
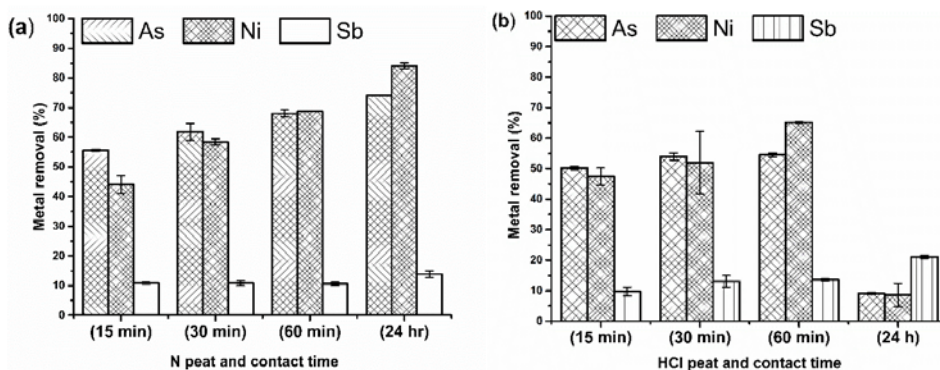
Figure 3. *Effect of time (23 ± 2 °C) on metal removal (%) from mining wastewater using (a) N peat and (b) HCl peat. 2 g/L dosage. 232 °C. Error bars represent max and min of experiment replicates.*

The effect of contact time at low temperature (5 °C) is shown in Fig. 4. The pH_{24h} of wastewater samples treated with HCl peat and N peat was around 6.2 and 6.8, respectively. The experiments at 5 °C had lower metal removal (%) than at room temperature for both sorbents. For N peat, As and Ni removal (%) increased with time; the optimum As (60%) and Ni (50%) removal was achieved at 60 min. However, no significant dependence on contact time was observed for HCl peat; although there was a slight increase in the amount of As removal at 60 min (55%) compared to 30 min contact time (50%).
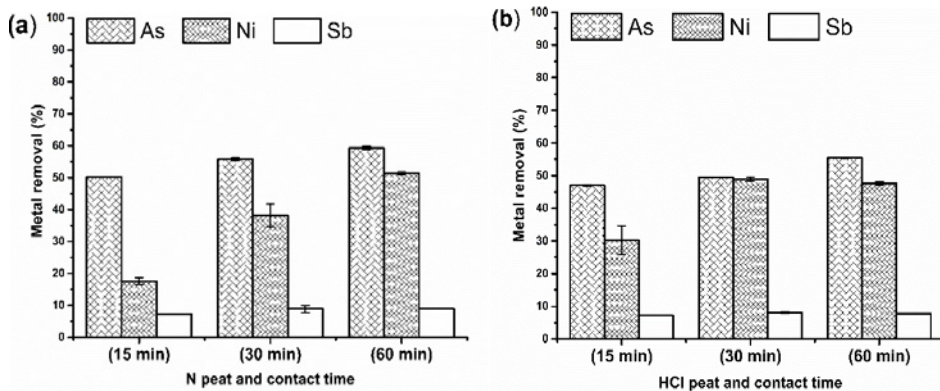
Figure 4. *Effect of time (5 °C) on metal removal (%) from mining wastewater using (a) N peat and (b) HCl peat. 2 g/L dosage. 5±2 °C. Error bars represent max and min of experiment replicates.*

Discussion

In this study, the metal removal performance of N peat and HCl peat was evaluated for the treatment of mining wastewater at different doses and contact times. Overall, N peat performance was clearly better than that of HCl peat. The aim of treating peat with HCl acid was to enhance the sorbent metal uptake capacity by altering its structure so that the functional groups present were more readily available for adsorbing metal ions. Furthermore, the goal was to improve the settling characteristics of the peat particles. Although not so significant in batch test conditions, enhancing the settling characteristics of peat would be very valuable in real applications. Visual observations pointed to an improved settling ability of HCl peat but its sorption capacity was lower than that of N peat throughout the study. The sorption efficiency of a sorbent for a particular metal depends on several factors such as the affinity of the metal ion towards sorption sites on the sorbent, composition and pH of the wastewater. The main functional groups in the peat responsible for metal uptake are considered to be the phenolic and carboxylic groups (as shown in FTIR results) provided by fulvic and humic acids, which are capable of rapid metal cation uptake in exchange for release of H^+ ions into the solutions (Brown, *et al.* 2000; Holub & Balintova 2014). Acidic treatment of peat contributed to a lower equilibrium pH of the treated wastewater, which can be related to release of hydrogen ions. Thus a straight comparison between the sorbents is difficult due to the different equilibrium pH values of the treated wastewater. Gosset *et al.* (1986) also reported that unsieved and unacidified samples of peat performed better in

copper removal compared to 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 species increased their Cr(III) uptake.

The sorption efficiency of peat towards different metals was observed to depend on the metal species present in the treatment solution. N peat and HCl peat exhibited high to moderate As and Ni removal but low Mn and Sb removal capacity. Studies have shown that this difference in metal ion affinity towards peat can be attributed to chemical properties such as the ionic potential, reduction potential and electronegativity of the metal ion among other factors. For example, the research by Liu *et al.* (2008) proved that the reduction potential of metal ions is related to their affinity to be adsorbed on peat. The standard reduction potential (E°) of As(V), Ni, Sb(V) and Mn are 0.560 V, -0.25 V, 0.605 V and -1.185 V respectively, which (except for Sb(V)) are in line with the findings of Liu *et al.* (2008), who stated that the higher the reduction potential, the higher the metal ion removal (%). Since the final pH of treated wastewater was found to be slightly acidic after the sorption experiments, the reduction potential of As and Sb for acidic solutions was considered. Speciation of As and Sb depends on the redox potential and pH; however, the particular oxidation states of As(V) and Sb(V) were assumed to be present in the studied wastewaters based on reports that As was present as arsenate [As(V)] and Sb predominantly existed as antimonite [Sb(V)] under oxidizing aerobic conditions such as in surface waters (Nicomel *et al.* 2015). Throughout our experiments, As and Ni were the most efficiently removed metals, followed by Sb with Mn. This is in agreement with the dependence of metal affinity towards peat on reduction potential. It is worth mentioning that the removal mechanism of metalloids (As and Sb) may be different than metal cations such as Ni, since metalloids are capable of co-precipitating as hydroxides with metals like Fe and Mn present in high concentrations in mining waters, but the extent of this co-precipitation mechanism is still not clear (Palmer *et al.* 2015).

Experiments studying the effect of contact time at 23 ± 2 °C indicated that, once equilibrium had been achieved, the HCl peat sorbent reached saturation and the elongated contact time led to metal desorption into the solution. This is particularly challenging for the treatment of changing water quality i.e., metal concentrations that fluctuate over time. In addition, contact time experiments conducted at 5 °C showed that temperature plays a key role in the sorption behavior of N peat while acid-modified peat was not significantly affected by the change in temperature.

Conclusions

From the batch sorption tests carried out to study the effect of dosage, contact time and temperature on the performance of natural and HCl-modified peat for the treatment of mining wastewaters, the following can be concluded:

1. N peat was a better sorbent than HCl peat. The equilibrium pH of HCl peat was considerably lower than that of N peat, thus the lower pH due to acid treatment coupled with the nature of the wastewater could have led to the lower sorption efficiency of modified peat.

2. Arsenic and nickel were the most efficiently removed metals by both N peat and HCl peat. Removal of Mn and Sb was very low in all sorption experiments except for the 4 g/L dosage of HCl peat, which removed around 50% Sb.

3. The sorbents performed better at 23±2 °C in comparison with 5±2 °C. The removal of As was fairly independent of contact time while Ni removal was highly dependent on contact time.

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