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Enhancing peat metal sorption and settling characteristics

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Abstract

Peat is an excellent material for metal sorption since it naturally contains different kinds of functional groups that can sorb metal cations from water. The main objective of this work was to test low-cost treatment (acid and alkali) methods for natural peat, which would improve the settling properties of peat particles while maintaining its metal removal efficiency. Particularly, the poor settling properties of peat hinder its practical application. The study revealed that NaOH-treated peat (0.1 M) had excellent settling properties and could be applied in wastewater applications having mixing and settling systems without a settling aid. The superior leaching of humic and fulvic acids in alkaline treatment caused a change in morphology, making it a harder and sticky material. Moreover, the NaOH-treated (0.1 M) peat was proven to be the most efficient material for nickel removal followed by the HCl-treated (0.2 M) peat, citric acid-treated (0.16 M) peat and water-treated peat. A higher

temperature and longer time slightly increased the Ni removal efficiency with NaOH-treated peat material. The settling of HCl-treated peat was studied further using polyacrylamide flocculants (cationic, neutral, anionic). Cationic flocculants performed best and the cationic charge density also had an effect on the flocculation performance of peat particles. This study provides further evidence that peat can be applied in the treatment of metal-containing wastewaters.

Keywords: Peat pre-treatment; Nickel removal; Characterization; Morphology; X-ray photoelectron spectroscopy; Flocculation

Introduction

Industrial wastewaters and urban run-offs contain metals that may cause serious effects on the environment even at low concentrations. Although a number of commercial water treatment methods have been developed, they are often expensive, have high energy and chemical demands, produce additional wastes and are incapable of treating dilute wastewaters (Araújo et al. 2013; Barakat 2011). Thus, in the light of these drawbacks, there is an urgent need to develop low-cost water treatment materials, which are environment friendly, abundantly available and are capable of efficient removal of metals even from a low concentration. Various biosorbents have been investigated for metal removal. For example, Vaseem et al. (2017) used successfully a macrofungi *Pleurotus ostreatus* for the treatment of toxic coal washery effluent.

Peat, a naturally forming biosorbent, abundantly found in water-logged and marshy lands, is a decayed plant material (Brown et al. 2000). The main constituents of peat are lignin, cellulose and organic acids (i.e. humic and fulvic acids). Thus peat contains a number of active functional groups (e.g. phenolic, sulphonic and carboxyl), which are able to sorb metal ions through chemical interactions. The metal removal efficiency of peat is highly dependent on pH (Ho et al. 1995). The main mechanisms of metal sorption by peat are ion exchange, complexation and adsorption (Ho et al. 1995; Gosset et al. 1986). In ion exchange, the metals cations react with the carboxyl acid groups on

the peat surface, which in turn release H^+ ions into the treated wastewater. Complexation reactions may involve the formation of inner sphere complexes (chelation of metal) or outer sphere complexes (electrostatic attraction) (Brown et al. 2000). Adsorption involves the attachment of metal cations on the surface without the exchange of ions or electrons (Brown et al. 2000).

The use of peat has been suggested for the removal of metals from wastewater. In wastewater treatment the use of peat poses certain challenges such as the poor mechanical properties and chemical stability of peat. Peat as such could deteriorate the water quality since it contains easily leachable humic material, i.e. humic and fulvic acids, which are a mixture of weak aliphatic and aromatic organic acids (Pettit 2004). In addition, peat does not settle well in water, which hinders its use in real applications. Therefore, some treatment is needed before applying peat in wastewater treatment. For example, Smith et al. (1976) studied the improvement of the physical characteristics of peat by treating it with phosphoric acid, which resulted in reduced leaching and swelling properties. Alkali-treated (Caramalău et al. 2009; Bulgariu et al. 2011) and sodium chloride-treated (Balan et al. 2009) peat materials have exhibited higher metal uptake capacities than natural peat, whereas nitric acid-treated peat showed a lower capacity than natural peat (Caramalău et al. 2009). In spite of various studies reporting metal removal capacities for natural (fresh) or modified peat samples, there is a lack of information regarding the settling behaviour of peat after treatment and how settling can be improved. The treatment should be cost-efficient and should not decrease the existing metal sorption capacity of peat. This paper focuses on how to solve the issue of settling. The specific aims were 1) to investigate simple peat treatment at 25 °C and at 60 °C using acids (hydrochloric acid and citric acid) or a base (sodium hydroxide) and compare it to treatment with pure water, 2) to measure nickel sorption capacity after treatment, 3) to investigate peat characteristics and settling behaviour after treatment, and 4) to determine a suitable flocculant for enhancing the settling of one peat material (HCl-treated peat).

2. Material and Methods

2.1. Treatment of peat

Peat was obtained from Stora Enso Veitsiluoto pulp mill (Finland), which burns peat for energy. The peat was dried at 80 °C for 24 h and then sieved to obtain a fraction of 90-250 µm, which was used in the experiments. The ash content of the obtained peat fraction was low: 6.22 % ± 0.04 % measured at 525 °C (ISO 1762:2001) and 5.62 % ± 0.04 % measured at 900 °C (ISO 2144:1997) using a Precisa prepASH 129 furnace. The low ash content is related to the small amount of inorganic substances such as mineral soil.

A full factorial design was chosen to investigate the peat treatment. The three factors investigated were chemical type (0.1 M NaOH (Sigma-Aldrich), 0.2 M HCl (Merck), 0.16 M citric acid (C₆H₈O₇, Sigma-Aldrich) and ultrapure); temperature (25 °C and 60 °C); and time (2 and 6 hour). Concentrations of chemicals were selected according to the literature and preliminary investigations. The yield of peat material and Ni removal efficiency (0.5 g/l dosage, see section 2.2.) were chosen as experimental variables. The results were evaluated by computing the coefficients using multiple linear regression (Modde 8.0 software, Umetrics AB). The coefficient was considered significant if the p value was below 0.05. The regression models for both responses are in the form:

$$y = b_0 + b_1X + b_2Y + b_3Z + b_{12}XY + b_{13}XZ + b_{23}YZ$$

where y is the response (yield or nickel removal), b₀ is the constant; b₁, b₂ and b₃ are coefficients of the coded variables X (chemical type), Y (temperature) and Z (time), respectively; and b₁₂, b₁₃, and b₂₃ are coefficients of the interaction effects between two variables. Three factor interactions were not included.

The treatment procedure was the following: Three grams of peat (90–250 µm) was added into a 50 ml solution (NaOH, citric acid, HCl or water) and mixed for two or six hours at a temperature of 25

°C or 60 °C. The peat sample was then washed well with ultrapure water and oven dried at 60 °C for 24 h, after which the yield was measured. All treatments were done with one repeat.

2.2. Batch sorption experiments

Batch sorption experiments were conducted by shaking a peat sample (dosage 2 g/l and 0.5 g/l) with 10 mg/l of synthetic nickel solution ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck) in a plastic bottle in a rotating shaker. The aim was to study the nickel removal efficiency at a constant dosage of 2 g/l. On the basis of the results, the experiments were also performed with a lower dosage of 0.5 g/l. The pH of the solution was adjusted at the beginning to 5–6 and readjusted after 1 h and 5 h if necessary. After providing a mixing time of 24 h at room temperature, the peat was separated from the sample by centrifugation (Jouan C4.12, 10 min, 2500 rpm). First, 10 ml was taken from the top of the supernatant for Ni analysis. Then, a sample was taken for pH analysis (referred to as the final pH) and for DOC (dissolved organic carbon) analysis (measured only with a peat dosage of 2 g/l).

On the basis of the nickel removal results, the maximum sorption capacity was investigated for the NaOH- and HCl-treated peat samples only. The maximum sorption capacity curve of the NaOH- and HCl-treated peat was obtained using a similar batch sorption procedure where a 1 g/l dosage of peat sample was shaken with 50 ml of the nickel nitrate solution (2–100 mg/l) for 24 hours at pH 5–6.

2.3. Peat settling

Peat settling in water as a function of time was investigated using jar-test equipment (Kemira), a dosage of 1 g/l and a sample volume of 500 ml. After a period of rapid mixing (200 rpm, 30 sec) followed by slow mixing (50 rpm 10 min), a settling time of 25 min was used. Turbidity measurements were performed on 30-ml samples collected at 1/3 depth and at pre-determined time

intervals during the settling. All turbidity values were taken 10 seconds after placing the sample in the turbidimeter.

The effect of adding flocculant to enhance the settling of HCl-treated peat was studied using cationic polyacrylamides (Superfloc C491 K, Superfloc C494 HMW, Superfloc C-498 HMW), anionic polyacrylamides (Superfloc A100 HMW, Superfloc A120 HMW, Superfloc A137) and a neutral polyacrylamide (Superfloc N-300), all obtained from Kemira. With the cationic products, the charge density increased as follows: C491 K < C494 HMW < C498 HMW. With the anionic products, the charge density increased as follows: A100 HMW < A120 HMW < A137. The jar-test equipment and 1 g/l dosage of HCl-treated peat were used in the experiments (pH = 4.1–4.3). The flocculant solution was added while mixing the peat sample rapidly (200 rpm for 30 s). The sample was then mixed slowly (50 rpm) for 10 min. It was allowed to settle for 10 min, and the turbidity measurement was performed on a 30-ml sample collected at 1/3 depth immediately after the experiment.

2.4. Water analyses and peat characterization

Nickel was analysed by flame atomic absorption spectrophotometry (Perkin Elmer AAnalyst 400) following standard method SFS 3047. DOC was measured with a Sievers 900 portable TOC analyser (GE Analytical Instruments). The wastewater was filtered with 0.45 µm filters prior to the DOC analysis. Turbidity was measured with a Hach Ratio XR (Hach Company) and pH was measured with a Metrohm 744 pH meter.

The morphology of the peat samples (treated at 25 °C for 2 hours) was studied at 5 kV, using field emission scanning electron microscopy (FESEM, Zeiss Sigma). The samples were mounted on the surface of ultra-smooth carbon adhesive tabs (12 mm diameter) placed on a disc. A thin layer of platinum (5–10 nm) was coated on the samples for charge dissipation during FESEM imaging. FESEM micrographs were taken at different magnifications.

X-ray photoelectron spectroscopy (XPS) spectra were carried out for the peat samples with a Thermo Fisher Scientific ESCALAB 250Xi using a monochromatic Al K α source (1486.6 eV). The peat samples were mounted on indium foil. The XPS spectra were taken from one sample location. The spectra were recorded perpendicular to the surface and the diameter of the analysed area was approximately 900 μ m. The wide-scan spectra were recorded in steps of 1 eV and with a pass energy of 150 eV, and the high-resolution spectra in steps of 0.1 eV and with a pass energy of 20 eV. 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 (BE) of adventitious carbon to 284.8 eV. The C 1s spectra were fitted using the Shirley background and the Gaussian-Lorentzian sum function.

3. Results and Discussion

3.1. Peat characteristics

The yield of the peat material was mainly affected by the leaching of components during treatment while some material loss might also have occurred during the washing stage. Figure 1 shows the yield obtained in the treatments. It shows that the NaOH treatment resulted in lowest yields and the temperature had significant effect on the yield (lower yield at higher temperature with NaOH). The statistical analyses applied to yield confirmed that the chemical type (NaOH) and the interaction between NaOH and temperature were significant (p value < 0.05) (Table S1). The other significant factors and interactions were water, citric acid-temperature and water-temperature. Water treatment resulted in higher yield and the temperature had a positive effect on yield with water and citric acid. Mixing peat with 0.1 M NaOH resulted in a dark brown liquid and washing filtrates, which is a consequence of the dissolution of humic and fulvic acids in alkaline conditions. The solid residue that was formed is presumed to have contained residual humic and fulvic acids, humin and inorganic substances. Humins are large macro-organic complexes that are insoluble in water at any pH (Pettit

2004). Higher temperature increased the dissolution of these components, although two hours seems to be sufficient with the molarity of NaOH and single-stage treatment used. Cook et al. (1998) showed that the leaching time had a greater effect on humic acid leaching than the molarity of the NaOH. On the other hand, successive extractions dissolve more humic acids and the insoluble humin content may be as low as 10–15% of the starting peat material (Chiou et al. 2000; Helal et al. 2016).

For other materials, the yield varied between 80 and 90% (Fig. 1). HCl and citric acid treatments also resulted in brown liquids but they were not as dark as with NaOH. HCl treatment dissolved at least part of the fulvic acids (Cook et al. 1998), which are soluble in all pH conditions whereas humic acids are insoluble in very acid conditions (Pettit 2014). Acid treatment can also replace the sorbed metal ions on peat with hydrogen ions and thus improve the sorption capacity of peat material (Caramlău et al. 2009). In addition, acid treatments may release inorganic ions such as Al, Fe, Ca, Mg and P while silicates and sulphur may remain insoluble (Zevenhoven et al. 2009).

The morphology of the NaOH-treated peat differed greatly from the others. It dried solid and had to be crushed for batch sorption and settling experiments. Bulgariu et al. (2011) reported that the most significant changes in the FTIR spectrum of the peat surface after alkaline treatment (0.5 M NaOH) as compared to fresh peat were observed in the region of 1730–1620 cm^{-1} . They concluded that alkaline treatment increased the dissociation degree of free carboxylic groups and hydrolysis of esters and another carboxylic acid compounds. Fig. 2 shows the FESEM images of the fresh peat and treated peat samples. The differences on the surfaces were observed from these micrographs. NaOH and HCl had a stronger impact on the peat surface: the surface was much smoother in comparison with citric acid-treated and water-treated peat samples. In addition, NaOH- and HCl-treated particles were agglomerated as a consequence of treatment whereas citric acid-treated and water-treated peat samples consisted of clearly smaller particles of several dozens of micrometres.

The surface of all the peat samples contained mainly carbon and oxygen with small amounts of nitrogen, iron and sulphur (Fe and S were detected only with high-resolution spectra) (Table 1).

NaOH-treated peat also had sodium on its surface, originating from the NaOH chemical, whereas HCl- and water-treated peat materials had some silicon. The appearance of Si on the surface of HCl-treated peat suggests (2.4 at.%) that silicates had previously been covered by organic material and were revealed to a great extent only by HCl treatment.

The C 1s spectra of the peat materials contained three peaks (Fig. S1, which were fitted as follows: aromatic and aliphatic carbon (C–C, C–H; 284.6 eV), carbon having a single bond with oxygen and nitrogen (C–O, C–N; 286.1–286.2 eV) and carbon having two bonds with oxygen (O–C–O, C=O; 287.9 eV). No significant changes were observed in the proportion of the different carbon components as a consequence of treatments. The nitrogen in peat materials was mainly in amide form according to the dominating single peak observed in the N 1s spectrum at 399.9–400.1 eV (not shown). Pyrrolic nitrogen would appear at the same BE (Kelemen et al. 2006), but it has been demonstrated with K-edge XANES (X-ray absorption near edge structure) spectroscopy (Vairavamurthy and Wang 2002) and ¹⁵N NMR (nuclear magnetic resonance) (Kelemen et al. 2006) that peat does not contain pyrrolic forms of nitrogen. Pyrrolic nitrogen will appear as the coalification process proceeds. Pyridinic nitrogen (398.6 eV) and quaternary nitrogen (401.4 eV) peaks may exist to some extent in peat materials and their amount also increases with coalification (Kelemen et al. 2006). In contrast, Vairavamurthy and Wang (2002) found only pyridine forms of nitrogen in addition to the amide form in the humic substances extracted from peat. The shoulder at the higher BE side (401.2–401.7 eV) for all peat samples with the exception of the NaOH-treated peat sample suggested the presence of quaternary nitrogen, which might act as anion exchange sites for anionic pollutants.

3.2. Nickel removal efficiency

The optimal pH reported for Ni sorption onto peat is between 4 and 7 (Ho et al., 1995; Bartczak et al., in press; Liu et al., 2008). At low pH (<3), hydrogen ions compete with nickel ions, although it was proved by Gosset et al. (1986) that nickel can strongly bind to peat even in very acidic media. At

pH values of higher than 8, the precipitation of nickel as hydroxide occurs. Therefore, our aim was to keep the final pH between 5 and 6 in all batch experiments. The final pH values are reported in Fig. 3. A 24-hour contact time was applied to confirm equilibrium even though low equilibrium times (≤ 60 min) have previously been reported (Liu et al. 2008; Bulgariu et al. 2011). The results of the current study show that different treatment methods have an effect on metal sorption efficiency.

All peat samples showed high removal efficiency for nickel (Fig. 3a) with the dosage of 2 g/l and initial Ni concentration of 10 mg/l. The efficiency of NaOH-treated peat increased as the modification temperature and time was increased, reaching 98% removal. HCl-treated peat removed >98% of nickel and the removal efficiency was unaffected by the temperature and exposure time. Peat treated with citric acid and water at high temperature for 6 h showed a lower removal efficiency (84% and 83%, respectively).

Since high removal rates were obtained with all peat materials at the dosage of 2 g/l, a lower dosage was investigated next. The experiments carried out with a lower dosage of peat material (0.5 g/l, Fig. 3b) showed that the NaOH-treated peat, whose capacities ranged between 16.9–19.5 mg Ni/g, was the most efficient material followed by the HCl-treated peat (14.9–18.9 mg Ni/g), citric acid-treated peat (14.4–16.4 mg Ni/g) and finally water-treated peat (13.2–14.4 mg Ni/g). The statistical analysis also confirmed that chemical type was a significant factor (Table S2). Also the interaction HCl-time showed a significant effect on Ni removal as the increase in the treatment time of peat with HCl decreased the Ni removal (with p value < 0.05).

Overall, the results obtained confirm the previous findings in the literature. Bulgariu et al. (2011) investigated metal removal with NaOH-treated peat (0.2 M) and showed that it had a higher Pb, Co and Ni removal capacity than that of natural peat, which was explained as originating from the higher availability of functional groups. They also showed that the sorption process was much faster with NaOH-treated peat (8 min) than with natural peat (60 min), which shows the additional benefit of NaOH treatment.

The sorption capacity was investigated for NaOH- and HCl-treated peat materials (2 hours at 25 °C) due to their better Ni removal efficiency when compared to citric acid and water treatments. The results confirmed that NaOH-treated peat is a more efficient product (Fig. 4). For NaOH-treated peat (25 °C, 2 hours), the obtained maximum capacity was 34.7 mg/g, which is consistent with a previous study (Bulgariu et al. 2011). HCl-treated peat achieved a lower capacity, 22.4 mg/g.

The DOC of the treated nickel solution after the batch experiment (2 g/l dosage of peat sample) was low with water-treated peat, which was probably not due to the pure peat material, but rather because of the low leaching effect of pure water (Fig. S2). The NaOH-treated peat at higher temperature showed a lower DOC, which implies that easily leachable humic material had been removed in the treatment. If peat material is to be used several times after regeneration, the leaching of organic matter would reduce over time. HCl (0.1 M) has been used successfully for nickel desorption from peat (Bartczak et al., in press; Bulgariu et al. 2011).

After peat treatment, the disposal of the extract should also be considered. It would be beneficial if the extract could be used for another purpose in order to avoid disposal as waste. The use of alkaline peat extract as fertilizer has been proposed, since humic substances provide a good source of organic carbon for plants (Saito and Seckler, 2014).

3.3. Settling of peat materials

Since natural peat does not settle well in water, the settling of the treated materials was studied as a function of time (Fig. 5). NaOH-treated peat showed the highest settling velocity. The high settling efficiency of NaOH-treated peat was due to the difference in morphology after treatment, as discussed in section 3.1. HCl-treated peat settled faster than water- and citric acid-treated peat (Fig. 5).

HCl-treated peat (25 °C, 2 h) was selected for further tests due to its good Ni removal efficiency but poor settling by gravity. In a real wastewater treatment application, poor settling can be overcome by applying flocculants. The flocculation performance depends on the dosage and nature of the

flocculant (molecular weight, charge density in the case of ionic polymers, polymer structure) and the quality of the treated suspension (e.g. amount and nature of particles and dissolved components, pH). A slight change in the treated suspension may determine which kind of flocculant performs best. The settling of HCl-treated peat was studied at pH 4.1–4.3, which is the pH that the HCl-treated peat had in water. Fig. 6 shows clearly that two cationic flocculants (C491 K and C494 HMW) stood out from the rest, which demonstrates the significance of charge density in the settling of peat. They clarified the water well at all tested dosages. Their cationic charge densities were lower than with the third tested cationic flocculant, C498 HMW, which did not perform as well. It is worth noting that the low turbidity value means that most of the peat material was at the bottom of the beaker, but there was also a minor amount on top of the water and on the walls of the beaker. Neutral and anionic flocculants did not work well and they also showed high deviation in the turbidity results. Nevertheless, it is worth bearing in mind that these experiments were carried out in pure water and studying only the interaction between peat material and flocculant. As mentioned above, the quality of the treated suspension may affect the flocculation performance. Before being applied to real wastewater, similar testing of different types of flocculants should be performed in order to optimize the treatment process.

The superior performance of cationic materials is associated with the negative surface charge of peat and thus the electrostatic attraction formed between the cationic polymer and peat particles. The negative charge of peat is related to the ionised organic functional groups. Bartczak et al. (2015) showed that the net negative surface charge increased with increasing pH, first steeply up to pH 6 and then mildly at higher pH values. The surface charge can also be affected by the amount and nature of the inorganic substances in the peat. For example, silicates generally have a net negative charge at pH values higher than 2–3 (Kosmulski 2014) whereas iron minerals have a net positive surface charge at acidic pH levels (Adegoke et al. 2011). In this case, the amount of inorganic compounds was low

according to the ash content. The iron and silicon contents on the surface were low according to XPS data. Thus the surface charge is probably mostly affected by the groups of organic matter.

4. Conclusion

This study has highlighted the importance of peat treatment before use in wastewater treatment applications. One of the major drawbacks of using peat is its poor settling properties, which had not been clearly recognized in previous studies. The main objective of this work was to test low-cost treatment methods for natural peat. The following criteria were used to rank the treatment methods: the nickel removal efficiency and settling behaviour of a treated peat sample and the removal of easily leachable humic material during the treatment. The results showed that NaOH treatment (especially at high temperature) leached humic material most efficiently and provided the most efficient peat product for nickel removal. Moreover, NaOH-treated peat settled the most efficiently and thus it would be easy to apply. The poor settling of peat materials (other than NaOH-treated) can be enhanced with flocculants. HCl-treated peat settled well with cationic flocculants. The cationic charge density of the flocculant affects the flocculation performance of peat particles. This work has proved that the use of treated peat samples in mixing and settling systems is feasible.

Acknowledgement

We wish to acknowledge Maa- ja vesitekniiikan tuki ry and the European Regional Development Fund (as part of the HuJa project, “Enhancing the treatment of metal containing storm waters and wastewaters by using natural materials) for funding the study.

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FIGURE AND TABLE CAPTIONS

Figures have been made by origin, except FESEM figures have been modified with GIMP (addition the title only).

Fig 1. Percentage yield obtained after treatment. Error bars show the maximum and minimum values of two experiment replicates.

Fig 2. FESEM images of NaOH-, citric acid-, HCl- and water-treated peat.

Fig. 3. Ni removal by peat, initial concentration of 10 mg/l, 24 h, initial pH 5.5 and dosage a) 2 g/l, b) 0.5 g/l. Error bars show the maximum and minimum values of two experiment replicates. The final pH with a dosage of 2 g/l: 5.7–7.1 NaOH, 4.3–5.5 citric acid, 5.0–5.6 HCl and 5.0–6.0 water. The final pH with a dosage of 0.5 g/l: 6.2–6.7 NaOH, 5.4–5.7 citric acid, 5.0–6.0 HCl, and 5.5–6.1 water.

Fig. 4. Sorption capacity of 0.1 M NaOH-treated peat and 0.2 M HCl-treated peat (treated for 2 hours at 25 °C). Equilibrium time 24 hours, final pH 4.4–6.2 with HCl-treated peat and 5.5–6.8 with NaOH-treated peat. Error bars show the standard deviation values of three experiment replicates.

Fig. 5. Settling of peat after treatment with 0.1 M NaOH, 0.2 M HCl, 0.16 M citric acid and water for 2 hours at 25 °C.

Fig. 6. Effect of flocculant dosage on the clarification of a water sample containing HCl-treated peat (25 °C, 2 h). Peat dosage 1 g/l, initial pH 4.1–4.3. The charge density increased as follows: C491 K < C494 HMW < C498 HMW and A100 HMW < A120 HMW < A137.

Table 1. Element content of peat surfaces as derived from XPS survey spectra (atomic %).