



## 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.

### 1. 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 waterlogged 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<sup>+</sup> 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 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

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capacity than natural peat (Caramalău et al., 2009 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 (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, Sigma-Aldrich) and ultrapure water); temperature (25 °C and 60 °C); and time (2 and 6 h). 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), b<sub>0</sub> is the constant; b<sub>1</sub>, b<sub>2</sub> and b<sub>3</sub> are coefficients of the coded variables X (chemical type), Y (temperature) and Z (time), respectively; and b<sub>12</sub>, b<sub>13</sub>, and b<sub>23</sub> 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 (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>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 h at pH 5–6.

### 2.3. Peat settling

Peat settling in water as a function of time was investigated using jar-test equipment (Kemira) and a sample volume of 500 ml. After a period of rapid mixing (200 rpm, 30 s) 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 s 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. A 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 sample 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 h) 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 Kα 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 µm. 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.

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