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ON THE ION-EXCHANGE PROPERTIES OF PEAT. PART IV: THE EFFECTS OF EXPERIMENTAL CONDITIONS ON ION EXCHANGE PROPERTIES OF SPHAGNUM PEAT

TURPEEN IONINVAIHTO-OMINAISUUKSISTA, OSA IV: KOEOLOSUHTEIDEN VAIKUTUS TURPEEN IONINVAIHTOKYKYYN

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The effects of experimental conditions on the ion exchange capacity of a column-shaped peat layer were studied. To make sure that the results were universal the columns were prepared from two peat types with strongly different cation adsorption capacities. The cation used was Cu^{2+}.

An increase in pH increased strongly the adsorption capacities in the pH range 1—5. Below the level of 200 ppm Cu^{2+} the capacity was to some extent dependent on concentration. Because of the rapidity of adsorption the flow rate and column height had practically no effect on the capacity.

The use of peat as an ion exchanger was studied by using a larger column prepared from the low-moor peat sample. The capacity was near the value reached with the smaller column and it remained nearly constant after repeated copper-adsorptions, elutions and washings. The maximum flow rate decreased in the beginning and reached a constant level rather soon.

The peat column worked like an ion exchange resin but the capacity was smaller. The results give an impetus to the use of larger peat columns made from selected, low moor peat for heavy metal filtration.

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INTRODUCTION

In this part we consider the influence of the experimental conditions on the ion exchange capacity of Sphagnum peat. The following factors will be under investigation: height of the column, flow rate, concentration and pH of the cation solution. Also the effect of repeated elutions on the ion exchange properties of a large column was studied.

The samples were selected so that they differed considerably in quality. The first sample was typical peat moss used for agricultural purposes (sample A) and the second sample represented a typical moss peat used in energy production (sample B). The degree of humification for sample A was H 1—2 and for sample B H 5—6 according to von Post's scale (1922). The peat mosses were mainly *Sphagnum* peat.

METHODS

The experiments were carried out using Cu^{2+} ions since its ion exchange properties are well-known, together with those of several other ions from our earlier studies (Tummavuori & Aho parts I and II 1980).

The ion exchange capacity was determined by the integration method. The samples were characterized by IR, thermogravimetry and elementary analysis.

The copper ion concentrations were determined by a Perkin-Elmer 5000 AA/ICP atomic absorption spectrophotometer. The copper nitrate stock solution was 1000 ppm by concentration and the pH was adjusted by nitric acid to the desired level.

A Perkin-Elmer Model 283 infrared spectrophotometer was used for the infrared analysis. The pellets for analysis were made from a mixture of 200 mg potassium bromide and 1 mg of dried and milled sample.

A Fisher TGA system Series 100 was used to record the thermograms. The samples used were 10 mg by weight, the flow rate of gases was 0.0022 dm^3s^{-1} and heating rate 0.167 K s^{-1}.

The pH was measured by an Orion Research pH meter, SCE reference electrode and a Beckman glass electrode.

The experimental colums were chromatographic columns of lenght 50 cm and diameter of 2 cm. The material of the columns was glass. An exact amount of peat with known moisture content was transferred to the columns. The apparatus is shown by Fig. 1.

The peat was carefully moistened in the column and air bubbles were removed by suction before the experiment. The test solution was poured into the column. The height of the solution was kept within 25—35 cm above the peat surface. The flow rate was measured manually with a stopwatch and the effluent was collected in 25 ml aliquots for analysis.

RESULTS AND DISCUSSION

Sample A contains 5.7 % hydrogen, 46.5 % carbon and 0.76 % nitrogen. The corresponding values for sample B are: 52.8 %, 5.8 % and 2.00 %. On the basis of ICP analysis the sulphur content was 0.28 % for sample A and 0.44 % for sample B.

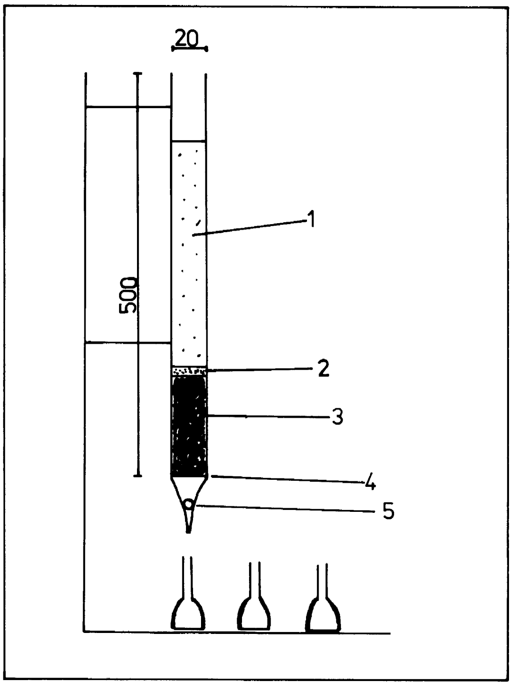

Figure 1. The apparatus used. 1. Cu^{2+}-test solution, 2. Glass wool plug, 3. Peat with air bubbles removed, 4. Ceramic porcelain 5. Precision stopcock.

Kuva 1: Käytetty laitteisto. 1. Cu^{2+}-liuos 2. Lasivillatuppo 3. Kostutettu turve, josta ilmakuplat on poistettu 4. Sintterisuodatin 5. Tarkkuushana.

TG-analysis gave volatile matter and ash contents of the samples. The volatile matter content of Sample A was 70 % and its ash content was 2.4 %. The corresponding values for sample B were: 57.5 % and 7.3 %. The TG analysis reveals that the reactivities of the samples are not identical. The logarithms of pre-exponential factors are: Sample A, log A=7.83 and Sample B, log A=7.55. The values have been calculated within the temperature range 450—750 K. The values of volatile matter were calculated from thermograms obtained in a nitrogen atmosphere and the values of other quantities were calculated from thermograms obtained in a mixed gas atmosphere (80 % N_2 and 20 $\%_2$) Tummavuori et al, parts I and II, 1978).

The most significant IR-adsorption areas of peat can be found at wavenumber regions

1600—1750 cm^{-1} and 1000—1200 cm^{-1}. The free carboxyl groups absorb at 1708—1727 cm^{-1}. These groups are able to bind metal ions. The adsorption at 1600—1650 cm^{-1} is due to the bound carboxylic groups. The range 1030—1085 cm^{-1} is important since alcohol and polysaccharide functional groups that may bind metal ions absorb in this range (Weast 1977—1978), Adhikari et al. 1970, 1978, Mathur et al. 1979, Schnitzer et al. 1972, Theng 1966).

The IR-analysis indicate clear differences between the samples. The signal of free carboxylic groups is stronger in the spectrum of sample A, which is in accordance with the stronger capability to bind metal ions when compared with sample B. The attachment of copper ions to peat at pH 3.0 is not clearly seen in the spectra because the proportion of the functional groups bound to copper is small in relation to the total amount of the free carboxyl groups. The spectra are shown by Fig. 2.

The mechanism of the ion exchange phenomenon does not appear to be the same in the different peat samples. Sample B has a scarcity of free carboxyl groups and the Cu adsorption that takes place is mainly a copper-metal cation exchange reaction. Sample A has, on the other hand, a larger proportion of free carboxyl groups and therefore high ion exchange capacity. So Cu adsorption reaction, after a certain degree of saturation, is mainly a copper-proton exchange (Fig. 3.).

The effect of the height of the peat column on the ion exchange capacity in the range 1—5 cm was studied. The capacity values are not dependent of the height of the peat column.

Because of the rapidity of the adsorption phenomenon the flow rate has no influence on the capacity in the range 1.6—6 ml/min (5—20 ueq/100 · s) Cu^{2+}.

Acidity has the greatest effect. pH-values from about 4.5 to 5.5 represent the range of buffer capacity in the moss peat. Below this range the ion exchange capacity decreases

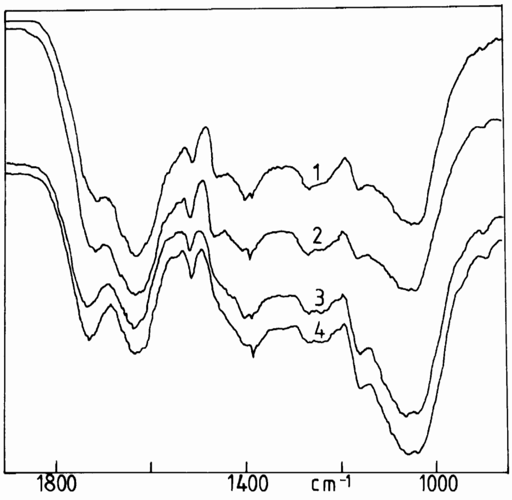

Figure 2. IR-spectra of the samples. 1. Sample B, 2. Sample B after treatment with copper solution 3. Sample A 4. Sample A after treatment with copper solution (100 ppm)

Kuva 2. Turvenäytteiden IR-spektrit. 1. Näyte B, 2. Näyte B. kupariadsorption jälkeen 3. Näyte A. 4. Näyte A kupariadsorption jälkeen.

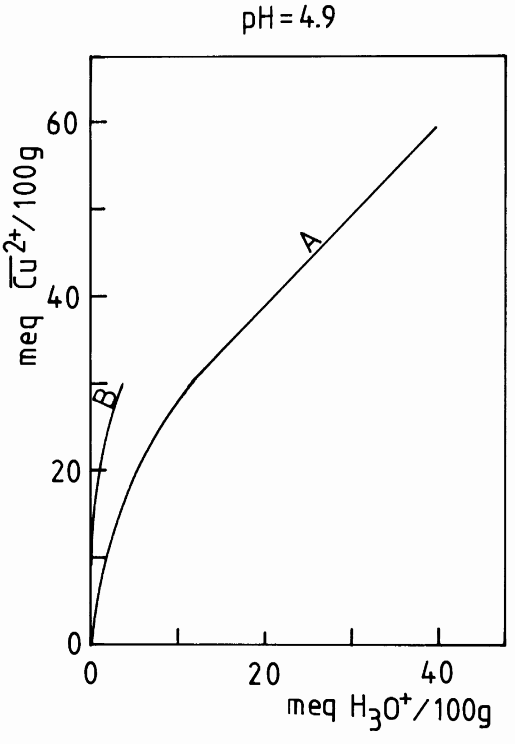

Figure 3. The release of protons from the peat as a function Cu adsorbed with a test solution of pH 4.9 from the two samples. X-axis: released protons (meq/100 g dry peat) Y-axis: bound copper (The capacity with sample A = 63 meq/100g and with sample B = 35 meq/100g).

Kuva 3. Ioninvaihtotapahtuman mekanismi pH:ssa 4.9 tutkituilla näytteillä. X-akseli: vapautuneet protonit (laskettuna mekv./100 g kuivaa turvetta) Y-akseli: Turvekerrokseen sitoutunut kuparimäärä (Näytteen A kapasiteetti 63 mekv./100 g ja näytteen B vastaava arvo 35 mekv./100 g.)

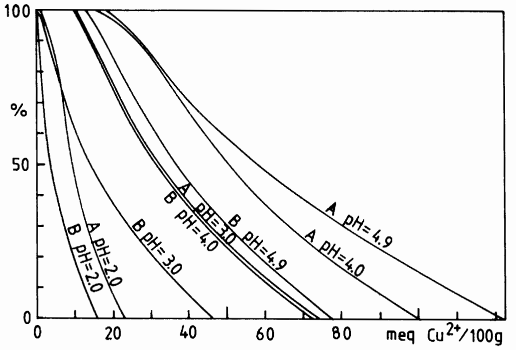

Figure 4. The adsorption curves for test solutions of different pH-values. The amount of Cu^{2+} added to the column. Y-axis: adsorbed part of copper (1 %).

Kuva 4. Adsorptiokäyrät, joista ilmenee pH:n vaikutus. X-akseli: turvepatsaaseen kulkeutunut kuparimäärä, Y-akseli: turpeeseen adsorboitunut kupariosuus tietyllä patsaaseen kulkeutuneella kuparimäärällä.

rapidly and above it pH increases the ion exchange capacity very effectively. The ion adsorption of the two samples responds to the pH of the test solutions differently due to the differences in the free carboxylic acid concentrations, as seen on the IR spectra. The adsorption curves of the pH-tests are shown in Fig. 4, and the corresponding capacity values in Fig. 5.

The Cu^{2+}-concentration in the test solution clearly influences the capacity below the level

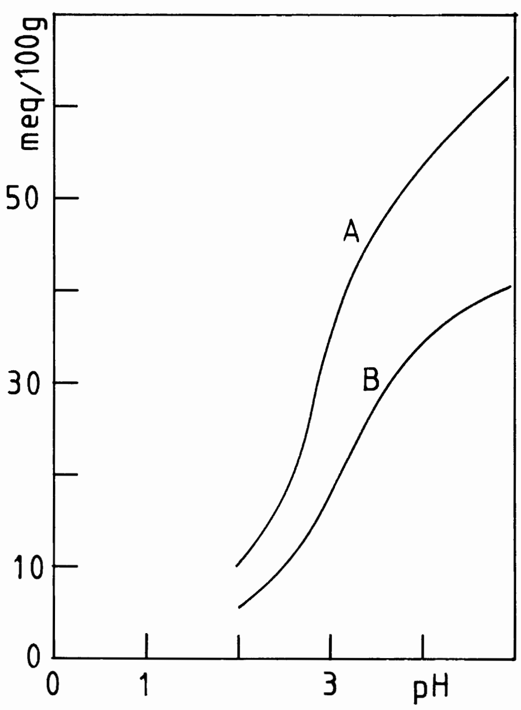

Figure 5. The effect of pH on the capacity values obtained from adsorption curves by graphical integration.

Kuva 5. pH:n vaikutus kapasiteettiarvoihin, jotka on laskettu kuvan 4. adsorptiokäyristä integroimalla ko. käyrän ja akseleiden väliin jäävä pinta-ala.

Table 1. Experimental conditions and capacity values

Taulukko 1. Koeolosuhteet ja saadut kapasiteettiarvot

sample	column height (cm)	pH	concentration (meq/l)	flow rate (μl/100gxs)	capacity (meq/100g
B	5.0	3.0	3.15 (100ppm)	2.5	18
B	2.3	3.0	3.15	4.5	22
B	1.2	3.0	3.15	8.7	23
A	5.0	3.0	3.15	4.9	36
A	2.7	3.0	3.15	10.3	39
A	1.4	3.0	3.15	19.5	40
B	5.0	3.0	3.15	4.6	18
B	5.0	3.0	3.15	9.2	17
A	5.0	3.0	3.15	10.0	38
A	5.0	3.0	3.15	20.3	36
B	5.0	3.0	6.30 (200ppm)	4.7	23
B	5.0	3.0	12.6 (400ppm)	9.2	25
A	5.0	3.0	6.30	9.9	43
A	5.0	3.0	12.6	19.8	47
B	5.0	4.9	3.15	2.3	40
B	5.0	4.0	3.15	2.3	35
B	5.0	2.0	3.15	2.4	5
A	5.0	4.9	3.15	5.0	63
A	5.0	4.0	3.15	5.0	54
A	5.0	2.0	3.15	4.9	11

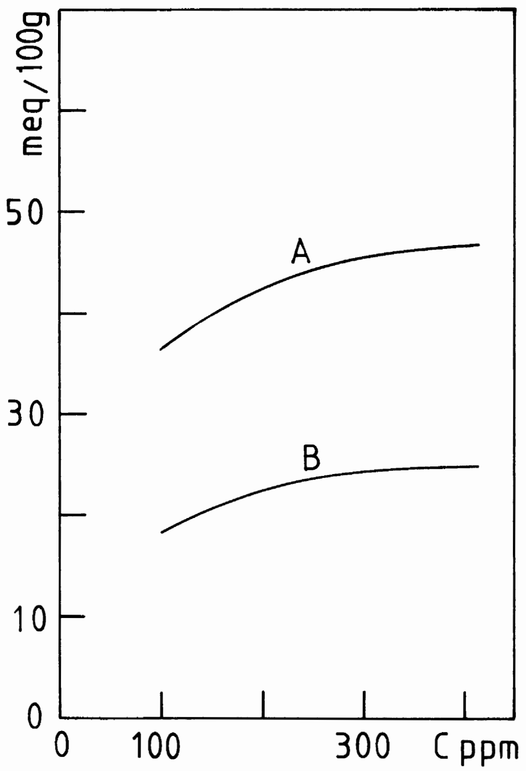

Figure 6. The effect of the Cu^{2+}-concentration in the test solution on the capacity.

Kuva 6. Liuoksen kuparipitoisuuden vaikutus kapasiteettiarvoihin.

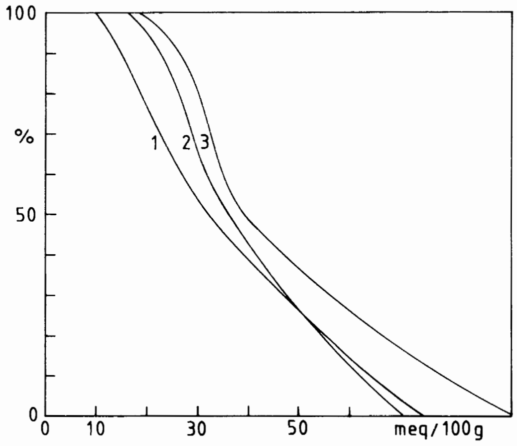

Figure 7. The average adsorption curves during the repeated use of the columns (580 cm^3) 2,3 and small column (16 cm^3) 1.

Kuva 7. Adsorptiokäyrät, jotka ilmaisevat keskimääräisen hajonnan suuruutta käytettäessä toistuvasti suurempaa (580 cm^3) turvepatsasta (käyrät 2 ja 3), sekä samalla näytteellä pientä patsasta käyttämällä saatu käyrä (1).

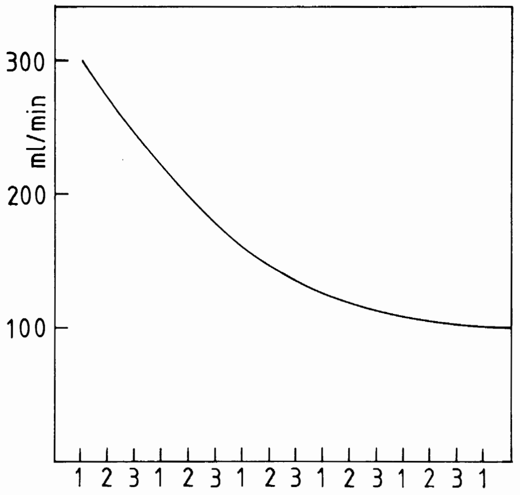

Figure 8. The effect of repeated use of the peat layer on the maximum flow rate of the effluent. 1 = Copper-adsorption stage, 2 = Elution by 1 M HNO_3, and 3 = Washing the column with distilled water.

Kuva 8. Toistuvan käytön vaikutus effluentin maksimivirtausnopeuteen. 1. vaihe: patsaan kyllästäminen kuparilla 2. vaihe: kuparin eluoiminen typpihapolla 3: vaihe: patsaan pesu tislatulla vedellä.

of 100 ppm Cu^{2+}. (Fig. 6.) The summary of all the experiments above as numbers is shown by Table 1.

We also made a column with a volume of 580 cm^3, that is about 35 times larger that the columns used above. The height of the peat layer was 19 cm and its diameter was 6.25 cm. When making large peat columns the degree of humification must be low in order to to obtain a suitable flow rate and therefore only sample A was used to make the larger column.

In this case the peat layer was treated like ion exchange resin, with repeated Cu^{2+}-adsorptions, elutions by 1M nitric acid and washings with distilled water. The factors under study were changes in the structure of the peat after repeated treatments, adsorption curves, elution profiles and the changes in the maximum flow rate. The effluent was collected in aliquots of 1000 cm^3. The elution profile of Cu^{2+} was determined in aliquots of 250 cm^3. The water volume of 1250 cm^3 was enough to wash out the attached copper.

It was found that the ion exchange capacity remained within narrow limits during repeated Cu^{2+}-adsorptions (e.g. Curves 2 and 3 in Fig. 7.) and the increase of the column from 16 cm^3 to 580 cm^3 infuences only slightly the adsorption curve (small column = Curve 1 in Fig. 7.)

The changes in the maximum flow rate of the effluent as a function of the amount of repeated treatments (adsorption, elution and washing) are seen in Figure 8. The height of the Cu^{2+} solution from the peat surface was kept constant. The compaction of suspended material decreased the maximum flow rate at the initial period of the experiments.

The absorbed part of the Cu^{2+} remains at high level (>99.5 %) until the adsorbed amount reaches the boundary value, 16—20 meq/100g. After that limit the adsorption percentage decreases continuously, the decrease obeying the first order kinetic equation.

The high adsorption level favours the use of low-moor peat as a cation filter. The cations adsorbed can be released with a small volume of acid and the layer can be repeately used. However, physical properties of the peat layer restricts the use of high flow rates of the effluent. In this study the maximum flow rate after several treatments was about one fifth from the volume of the layer per minute.

The experiments give an impetus to the study of still larger peat columns for heavy metal filtration, especially the changes in maximum flow rate during repeated use of the column, and the selection of the peat. Economical calculations are also needed when comparing the costs and adsorption capacity with ion exchange resins.

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TIIVISTELMÄ:

TURPEEN IONINVAIHTO-OMINAISUUKSISTA OSA IV: KOEOLOSUHTEIDEN VAIKUTUS TURPEEN IONINVAIHTOKYKYYN

Turpeen ioninvaihto-ominaisuuksia käsittelevän tutkimuksen osajulkaisussa 4 on tutkittu turvepatsaan ioninvaihtokykyyn liittyviä päätöksiä: patsaan korkeutta, virtausnopeutta, liuosväkevyyttä ja happamuutta. Artikkeli sisältää myös tuloksia suuremman mittakaavan kokeesta, jossa turvetta on käytetty kuten ioninvaihtomassaa.

Kaikki päätekijöiden vaikutusta käsittelevät kokeet tehtiin kahdella ioninvaihto-ominaisuuksiltaan suuresti eroavalla turpeella, jotta saatu aineisto olisi yleispätevä. Tarkasteltava kationi oli Cu^{2+}.

Liuoksen pH-alueella 1—5 pH:n nostaminen kasvatti voimakkaasti ioninvaihtokapasiteettia. Liuoksen väkevöityessä kapasiteetti nousi jonkin verran. Koska adsorptioilmiö on nopea, patsaan korkeudella ja virtausnopeudella ei ole juuri mitään vaikutusta kapasiteettiin. Jos patsas on hyvin matala, oikovirtausten vaara kasvaa.

Tutkittaessa turpeen käyttöä ioninvaihtomassana, paremmin adsorboivasta ja vettä läpäisevästä turpeesta tehtiin 36 kertaa normaalia suurempi patsas ja kerrosta käsiteltiin toistuvasti kationiliuoksella, eluentilla ja vedellä. Ioninvaihtokapasiteetti ei poikennut huomattavasti pienellä patsaalla saadusta arvosta ja se pysyi melko hyvin vakiona toistuvien käsittelyjen aikana. Sitoutunut kupari irtosi terävästi pienellä määrällä typpihappoa. Patsaan pH palautui nopeasti oikealle alueelle pienellä vesimäärällä. Koesarjan alkuvaiheessa patsaan fysikaalinen tila muuttui jonkin verran jolloin maksimivirtausnopeus pieneni. Maksimivirtausnopeus vakioitui myöhemmin. Lopputila oli suhteellisen hyvin vettä läpäisevä, toimiva ioninvaihdin. Tulokset rohkaisevat suuremman mittakaavan kokeisiin hyvin valikoidulla, vähän maatuneella turpeella.