

THE ION EXCHANGE PROPERTIES OF PEAT. PART V: ION EXCHANGE PROPERTIES OF SOME SPHAGNUM PEATS

TURPEEN IONINVAIHTO-OMINAISUUKSISTA. OSA V: ERÄIDEN SPHAGNUM TYYPPISTEN TURVELAJIEN IONINVAIHTO-OMINAISUUDET

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Normal milled peat contains different species of *Sphagnum*-peat. Five typical *Sphagnum*-peats were chosen for study in order to investigate differences in their ion exchange properties. IR-spectrum and TG-analysis reveal a great difference in the structure of the peat samples. Differences in the elemental composition does not effect on the ion exchange capacities. The ion exchange capacities of the different peat samples differ from each other *S. fuscum* having the largest capacity. This can be seen in IR-spectra at wave number region 1708—1727 cm^{-1} . When the test solution first flows through the column the adsorption percentage is high but after a certain moment, the adsorption percentage decreases. The decrease obeys the first order kinetics.

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INTRODUCTION

In our previous study we have found that the ion exchange capacities of peat moss from different production areas differ remarkably from each other depending on the degree of humification and the bog type. To clarify the factors affecting the ion exchange ability of peat we have studied ion exchange properties of some main types of *Sphagnum* peat.

There are many difficulties in investigating the ion exchange properties of peat. The main problems are the heterogeneity of the peat, variable chemical and physical properties of peat types and the various possible pretreatment methods. Similar research work can be carried out in a number of ways, which causes great diversity in the results obtained by different researchers. Thus comparison of the

results given by different authors is difficult and sometimes impossible.

The two principal methods that can be used when investigating the ion exchange properties of peat are as follows:

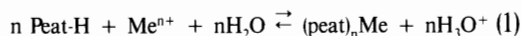
- Peat is titrated with sodium hydroxide and pH is measured. The consumption of sodium hydroxide gives an estimate of the ion exchange capacity equivalent of peat in alkaline solution.
- Peat is converted to the proton form and mixed with the solution of metal ions to be investigated. The amount of metal cation adsorbed by peat is determined either directly by measuring the metal content of the solution or indirectly by measuring the protons released by metal

cation exchange (Puustjärvi 1956, 1968, Thorpe 1973).

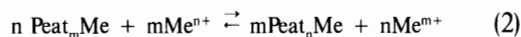
The equilibria can be either static, which can be accomplished by shaking a known amount of peat in the metal solution, or dynamic, which are accomplished by allowing a solution of known concentration to flow through a peat column. The latter approach has been used in our study (Tummauori and Aho 1980, parts I & II, Tummauori et al 1983).

In the kinetic method there is an excess of peat with respect to the metal ions so that the equilibrium is not reached, and the adsorption of metal ions is measured as a function of time (Bunzl 1974, parts II, III, IV).

If the pH of the solution under investigation is low enough (i.e. there is no metal hydroxide formation) one can describe the ion exchange events as follows:



If peat is incompletely protonated the metal ions of untreated peat are exchangeable, too:



This reaction occurs if the adsorption capabilities of two metal ions differ significantly. So the ion of stronger binding ability replaces the weaker ion in the peat.

We have used elementary analysis, IR spectrophotometry and thermogravimetry to describe some differences in the structures of the peat samples.

Three cations were used for the ion exchange studies: potassium, calcium and copper. The potassium ion represents alkali metals, calcium alkaline earth metals and copper is a transition metal with strong complexing ability and, as such, a good measure of chemical binding.

MATERIAL AND METHODS

The studied subsamples, collected from Central Finland, represented the following peats: *S. cuspidata* peat (H 1—2), *S. palustris* peat (H 1—2), *S. fuscum* peat (H 2), *S. cuspidata* peat (H 3) and *S. fuscum* peat (H 3). The numbers in parentheses represent the degree of humification by von Post (von Post 1922). The wet samples were sent and the identification was performed by authors in State Fuel Centre (VAPO).

The treatment of samples, experimental conditions and chemical analysis have been previously described (Tummauori & Aho 1980, parts I and II).

For the determination of the total individual metal contents of the subsamples they were first ground and 0.5 g of the sample was wet digested in a teflon bomb. The digestion solution was HF — HNO₃ — HClO₄ (6:4:1) for manganese, iron, copper and potassium, and HNO₃ — HClO₄ (4:1) for calcium and strontium. The acids used were concentrated and the total volume of the mixture used in each teflon bomb was 10 cm³.

The peat layer used in the chromatography column was about 5 cm in height and about 16 cm³ by volume. The flow rate through the sample was 1.5 cm³ min⁻¹.

Concentrations of the test metal solutions were: K 50 ppm, Ca 50 ppm Cu 100 ppm, and 5 × 10⁴ with respect to HNO₃.

The atomic absorption spectrophotometer was Perkin-Elmer model 5000/ICP. The thermobalance was Fisher Series TG 100, and the gas flow in thermogravimetric experiments was 0.0022 dm³min⁻¹ for nitrogen and mixed gas (80 % N₂ and 20 % O₂). The IR spectrometer was Perkin-Elmer Model 283.

The contents of hydrogen, carbon and nitrogen were determined by Keskuslaboratorio Oy, Espoo, Finland.

RESULTS AND DISCUSSION

The element contents of the peats are shown by Table 1. The concentrations of the metals have been reported as g/g dry peat. The concentrations of hydrogen, sulphur and carbon are reported as per cent dry weight of peat. The element contents of the peat species under investigation are remarkably different. The concentrations of potassium, iron and nitrogen vary considerably. This is due to varying nutrient concentrations in the growing places of the moss types (Pakarinen 1982).

When using thermogravimetric analysis we calculated the values of thermodynamic parameters by the methods of Coats and Redfern (1964) and Broido (1969). The results are in Table 2. There is not clear differences in initial and final temperatures when comparing the values of the peat types. The reaction occurs within the temperature limits 440 K — 570 K. The mass loss is smallest with *S. fuscum* peat (H2, code 2) and with *S. cuspidata* peat (H3, code 3). The temperature range in the first reaction, which is mainly due

Table 1. The metal contents of the samples.

Taulukko 1. Näytteiden metallipitoisuudet.

Peat Sample	H	$\mu\text{g/g}$ dry peat								Percentage		
		Code	K	Ca	Sr	Mn	Fe	Cu	Zn	H	C	N
S. cuspidata	1—2	1	4730	1060	6,3	56	1480	41	79	6,0	44,5	1,09
"	3	2	1270	806	7,5	56	740	13	33	6,2	47,1	1,07
S. fuscum	2	3	340	1240	4,5	34	610	10	24	6,0	46,0	0,39
"	3	4	170	1530	5,8	29	4530	4	25	5,9	45,9	0,42
S. palustris	1—2	5	2960	1950	12,3	80	2320	33	71	6,0	45,5	0,71

Table 2. The kinetic quantities of the samples calculated from thermogravimetric curves. Codes: w = mass loss in the reaction, T_i = initial and T_f = final temperature of the reaction, E^* = activation energy (kJ/mole), $\log A$ = frequency factor.

Taulukko 2. Termogravimetrisistä käyristä laskettuja kineettisiä tekijöitä. Merkinnät: w = massahäviö reaktiossa, T_i = lämpötila reaktion alussa T_f = reaktion loppulämpötila, E^* = aktivoitumisenergia (kJ/mol) ja $\log A$ = Arrheniuksen yhtälön frekvenssitekijä.

Peat Sample	Code	K			Method Broido			Method Core		
		T_i	T_f	Δw	E^*	$\log A$	R	E^*	$\log A$	R
S. cuspidata	1	440	569	65	92	6,4	1,000	82	5,4	1,000
"	2	459	573	50	103	7,5	1,000	94	6,6	1,000
S. fuscum	3	437	553	44	105	8,2	0,997	99	7,6	0,999
"	4	447	571	61	99	7,2	0,995	92	6,4	0,995
S. palustris	5	462	573	62	117	8,8	0,996	107	7,9	0,997

to the pyrolysis of cellulose and hemicellulose of the moss types is relatively narrow, and the reactions are vigorous as is easy seen from the values of E^* and $\log A$. The peat types cannot be classified logically according to these parameters, because the degree of humification also has a significant effect on the thermograms.

The thermograms of the samples in mixed gas atmosphere are shown by Figure 1. The shapes of the curves are apparently dependent on the peat type. The thermograms are almost identical in nitrogen gas.

IR analysis reveals differences in the functional groups of the peats. The ion exchange properties are dependent on the amount and quality of certain functional groups. The IR-spectra of the peats under investigation are shown by Figure 2. The wave numbers, cm^{-1} , of the most significant adsorption bands are 1708—1727 cm^{-1} for C = O of COOH and ketones, 1611—1632 cm^{-1} for aromatic C = C, H-bonded C = O of COOH and COO, 1509—1522 cm^{-1} for aromatic C = C, 1369—1380 for aliphatic CH and COO, 1220—1263 cm^{-1} for C = O stretching and deformation of COOH, 1030—1083 cm^{-1} for C = O in cyclic aliphatic esters and alcohols (Adhikari et al. 1973, Mathus et al. 1978, Theng et al. 1966, Weast 1977—78). The dif-

ferences in the spectra of the various peats are relatively small. In this work the most important differences in the absorbances can be found within the ranges 1708—1727 cm^{-1} and 1611—1632 cm^{-1} , because the metal ions are bound to the peat mainly via the non-conjugated (free) carboxyl groups.

The ion exchange capacities of the peats under the conditions used were determined by integrating the area between X and Y axis and the adsorption curve from a plat, where the percentage of bound metal ions at time t is presented against the corresponding total amount of metal ions flown into the sample layer (meq/100 g dry peat) (Tummavuori & Aho 1980, parts I and II).

The adsorption curves for the metal ions tested are shown in Figures 3, 4 and 5. They reveal that both the quality of the cation and the species of peat effect the curve shapes.

The values of the calculated ion exchange parameters are listed in Table 3. When taking into account the degree of humification, *S. fuscum* and *S. palustris* peats have roughly equal ion exchange capacities. *S. cuspidata* peat is a weaker adsorber. Some of the peat species contain remarkably high amounts of potassium (see Table 1.). Potassium cannot be released at pH 3.3 which means that the values for the adsorption capacities of

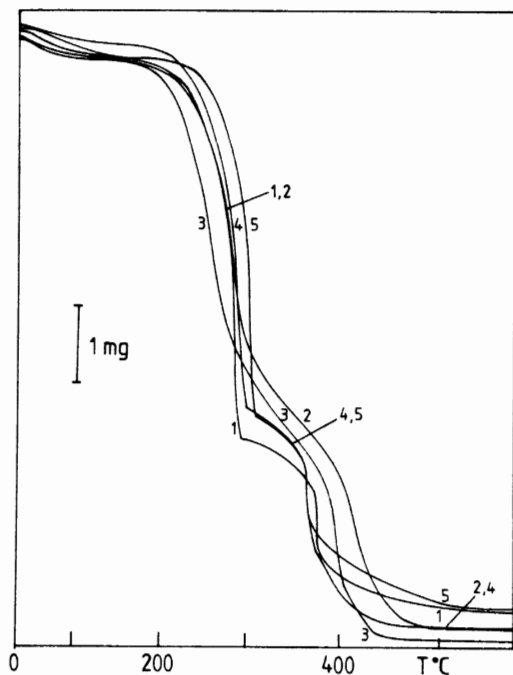


Figure 1. The thermograms of the samples in a mixed gas atmosphere.

1 = *S. cuspidata* -peat (H1-2), 2 = *S. cuspidata* -peat (H3), 3 = *S. fuscum* -peat (H2), 4 = *S. fuscum* -peat (H3), 5 = *S. palustris* -peat (H1-2).

Kuva 1: Näytteiden termogravimetriset käyrät seoskaasussa.

1 = *S. cuspidata* -turve (H1-2), 2 = *S. cuspidata* -turve (H3), 3 = *S. fuscum* -turve (H2), 4 = *S. fuscum* -turve (H3), 5 = *S. palustris* -turve (H1-2).

potassium are not proportional to the original potassium content of the peat.

The ratio of the absorbance of unconjugated carboxyl groups to the absorbance of conjugated groups can be regarded as a rough estimate of the ion exchange capability. The greater the ratio the greater is the adsorption capacity. This is shown by Figure 2 and Table 3 when comparing the data of *S. fuscum* peat with that of *S. cuspidata* peat. IR analysis is a useful method, because only physical methods such as grinding and pressing are needed for preparing the samples.

Pseudomolecular reactions obey the first order kinetics law in many cases as can be seen also from the shape of the descending part of the adsorption curve. The common first order equation has been used in our calculations:

A → products, or

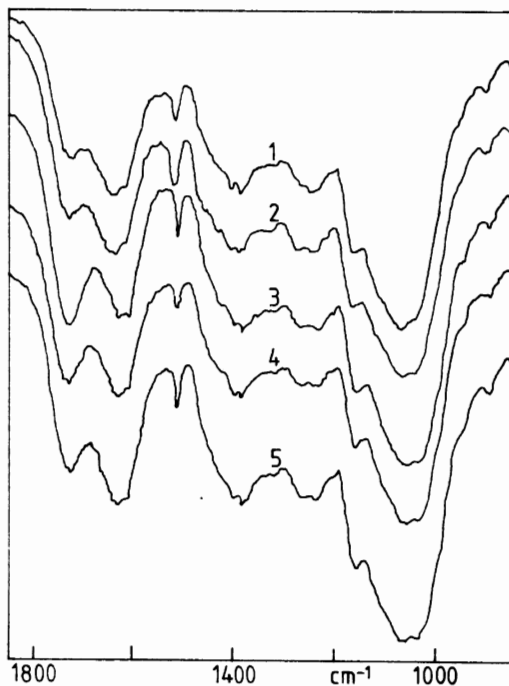


Figure 2. The IR-spectra of the peat samples.

1 = *S. cuspidata* -peat (H1-2), 2 = *S. cuspidata* -peat (H3), 3 = *S. fuscum* -peat (H2), 4 = *S. fuscum* -peat (H3), 5 = *S. palustris* -peat (H1-2).

Kuva 2. Näytteiden IR-spektrit.

1 = *S. cuspidata* -turve (H1-2), 2 = *S. cuspidata* -turve (H3), 3 = *S. fuscum* -turve (H2), 4 = *S. fuscum* -turve (H3), 5 = *S. palustris* -turve (H1-2).

$$\log(a-x) = -\frac{k}{2.3} t + C \quad (3)$$

where a is the maximum adsorption capacity under the conditions used (meq/100 g dry moss), x is the amount of bound metal ions at time t . The half life of the reaction is calculated from the equation:

$$t_{1/2} = \ln 2/k \quad (4)$$

The results are shown by Table 3. The experimental findings obey the law of first-order kinetics fairly well (regression coefficient nearly 1) although the system consists of two phases. This is probably due to the balancing effect of the high, practically constant water content and the constant amount of peat.

If we consider only the descending part of the adsorption curves, the calculated rates describe the adsorption profile of the metal ion on the peat below the adsorption level

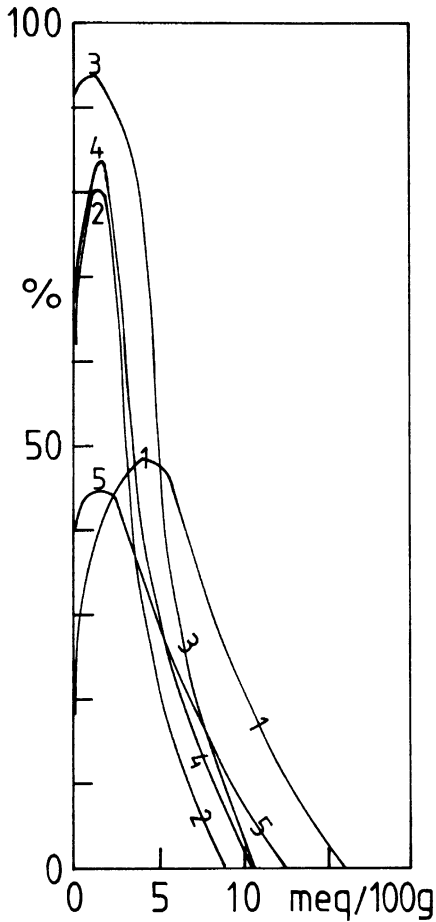


Figure 3. The adsorption curves of potassium.

1 = *S. cuspidata* -peat (H1-2), 2 = *S. cuspidata* -peat (H3), 3 = *S. fuscum* -peat (H2), 4 = *S. fuscum* -peat (H3), 5 = *S. palustris* -peat (H1-2).

Kuva 3. Kaliumin adsorptiokäyrät.

1 = *S. cuspidata* -turve (H1-2), 2 = *S. cuspidata* -turve (H3), 3 = *S. fuscum* -turve (H2), 4 = *S. fuscum* -turve (H3), 5 = *S. palustris* -turve (H1-2).

$\geq 99.5\%$. The flow rate of the cation test solution effects the values of k and $t_{1/2}$ and it is difficult to keep it as a constant rate for all samples, thus making the direct comparison of the values obtained complicated. However, in general, the greater the absolute value of k the greater the portion of the cations passing through the peat bound to the sample. When comparing the different cations, the absolute values of k are the greatest with copper and smallest with potassium. Correspondingly the values of $t_{1/2}$ correlate with the binding ability of ions within the descending part of the ad-

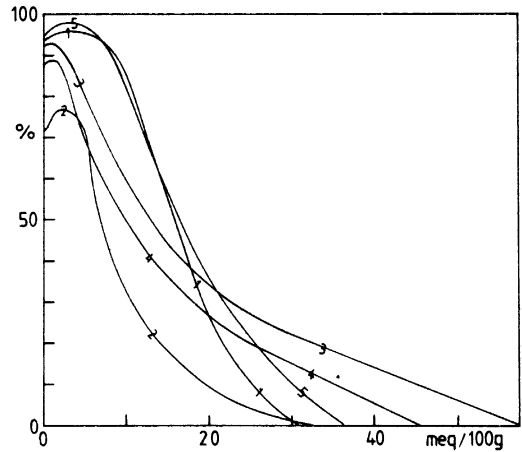


Figure 4. The adsorption curves of calcium.

1 = *S. cuspidata* -peat (H1-2), 2 = *S. cuspidata* -peat (H3), 3 = *S. fuscum* -peat (H2), 4 = *S. fuscum* -peat (H3), 5 = *S. palustris* -peat (H1-2).

Kuva 4. Kalsiumin adsorptiokäyrät.

1 = *S. cuspidata* -turve (H1-2), 2 = *S. cuspidata* -turve (H3), 3 = *S. fuscum* -turve (H2), 4 = *S. fuscum* -turve (H3), 5 = *S. palustris* -turve (H1-2).

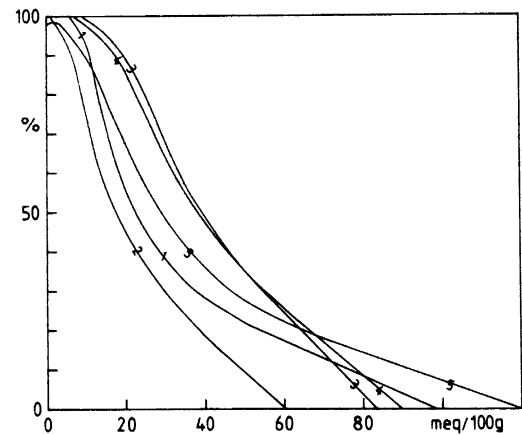


Figure 5. The adsorption curves of copper.

1 = *S. cuspidata* -peat (H1-2), 2 = *S. cuspidata* -peat (H3), 3 = *S. fuscum* -peat (H2), 4 = *S. fuscum* -peat (H3), 5 = *S. palustris* -peat (H1-2).

Kuva 5. Kuparin adsorptiokäyrät.

1 = *S. cuspidata* -turve (H1-2), 2 = *S. cuspidata* -turve (H3), 3 = *S. fuscum* -turve (H2), 4 = *S. fuscum* -turve (H3), 5 = *S. palustris* -turve (H1-2).

Table 3. The ion exchange capacities and the calculated kinetic parameters of the samples.
R = Regression, $t^{1/2}$ = half-life.

Taulukko 3. Näytteiden ioninvaihtokapasiteetit ja lasketut kineettisten tekijöiden arvot.
R = regressio, $t^{1/2}$ = puoliintumisaika.

	Code	Metal ion	Exchange capacity meq/100 g	-log k eq. (3)	$t^{1/2}$ (s) eq. (4)	R
S. cuspidata	1	Cu ²⁺	33	3.584	3210	0.999
"	2	"	23	3.699	3470	1.000
S. fuscum	3	"	43	3.873	5170	1.000
"	4	"	43	3.896	5440	1.000
S. palustris	5	"	39	3.600	2760	1.000
S. cuspidata	1	Ca ²⁺	16	3.181	1050	0.997
"	2	"	8	3.278	1310	0.996
S. fuscum	3	"	18	3.770	4080	0.999
"	4	"	14	3.689	3390	1.000
S. palustris	5	"	18	3.299	1380	0.999
S. cuspidata	1	K ⁺	4	3.237	1200	0.996
"	2	"	3	3.066	810	1.000
S. fuscum	3	"	5	3.181	1050	0.999
"	4	"	4	3.296	1370	0.999
S. palustris	5	"	3	3.114	900	0.999

sorption curve.

It is concluded, that neither adsorption capacity nor kinetic quantities alone can describe the ion exchange properties of peat, but one must also use the physical constants, mentioned above, for evaluating peat as ion exchanger.

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SELOSTE:

TURPEEN IONINVAIHTO-OMINAISUUKSISTA. OSA IV: ERÄIDEN SPHAGNUM TYYPPISTEN TURVELAJIEN IONINVAIHTO-OMINAISUUDET

Jyrsinturve koostuu tavallisesti useista turvelajeista, mistä syystä tässä osassa turpeen ioninvaihto-ominaisuuksia käsittelevää sarjaa on tutkittu muutamien *Sphagnum*-turpeiden ioninvaihto-ominaisuuksia.

Jotta syyt mahdollisille eroille adsorptiokyvyissä selviäisivät, näytteiden rakennetta tutkittiin IR-spektrometrian ja termogravimetrian avulla. Turpeen IR-spektrit ovat suhteellisen yksinkertaisia ja ioninvaihto-ominaisuuksien kannalta tärkeät vapaat ja sitoutuneet karboksyylyiryhmät näkyvät spektrissä hyvin.

IR-spektrien perusteella (aaltolukualue 1708—1727) voidaan ennustaa *S. fuscum*-turpeen suuri pyrkimys adsorboida kationeja. Koetulokset kationiliuoksilla vahvistavat asian. Näytteiden alkuperäinen kationipitoisuus ei vaikuttane kapasiteettiin. Kationien adsorboituminen näytteen läpi valuvasta liuoksesta turpeeseen on aluksi voimakasta. Tietyn kationimäärän jälkeen adsorptio alkaa heikentyä. Heikentymisnopeus noudattaa ensimmäisen kertaluvun kinetiikkaa.