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ON THE ION-EXCHANGE PROPERTIES OF PEAT
PART I: ON THE ADSORPTION OF SOME DIVALENT METAL IONS (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} AND Pb^{2+}) ON THE PEAT

TURPEEN IONINVAIHTO-OMINAISUUKSISTA
OSA 1: ERÄIDEN 2-ARVOISTEN METALLI-IONIEN ADSORPTIO TURPEESEEN

Ions can be classified into four groups with respect to their ion-exchange properties:

1. monovalent alkali metals, which are unhydrolyzable in aqueous solutions
2. divalent earth-alkali metals, which are weakly hydrolyzable in aqueous solutions
3. metals, which hydrolyze in aqueous solutions and some of them, particularly transition metals, possessing strong complex forming capabilities
4. anions.

In the main the following methods have been used in the investigations of the ion-exchange properties of peat:

1. Peat is titrated with sodium hydroxide and pH is measured. The consumption of sodium hydroxide gives an estimate of the equivalent ion-exchange capability of peat (Puustjärvi 1956, Puustjärvi 1973, Thorpe 1973).
2. Peat is converted to the proton form and stabilized with the solution of metal ions to be investigated. The amount of metals adsorbed by peat is determined either directly from peat or by the measurement of the protons released by metal ions. The equilibrium can be either static, which is accomplished by shaking the known amount of peat in the metal solution for a constant period of time, or dynamic; this is accomplished by allowing the solution of known concentration to flow thourgh the peat until the equilibrium is reached (Puustjärvi 1956, 1968).
3. The kinetic method uses the excess of peat with respect to the metal ions and measures the adsorption as a function of time (Bunzl, Schmidt, Sansoni 1976).

If peat is in proton from, the ion-exchange in aqueous solutions can be described as:

$$n\ \text{Peat-H} + Me^{n+} + n\ H_2O = (\text{Peat})_n Me + nH_3O^+ \qquad (1)$$

If peat is untreated of we have a mixture of metal ions an additional ion-exchange between metal ions may take place

$$n\ \text{Peat}_m Me + mMe^{n+} = m\text{Peat}_n Me + nMe^{m+} \qquad (2)$$

A comparison of the results given by several authors is difficult to assess due to the different methods of investigation and due to the different pretreatment methods of peat. Some use air-dry peat, some absolute dry. In some cases peat is powdered by milling or cutting or sieved only to remove the finest fractions. To remove soluble metal compounds a water-alcohol mixture is commonly used the peat is powdered thereafter. Only a little information is available concerning the peat types or the degrees of humification, except in the case of moss peat where the investigations have been carried out in controlled conditions

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(Puustjärvi 1956, Puustjärvi and Robertson 1975).

As a reference material, some laboratories have used pure humus prepared in the laboratory or various fractions of the soil extracts (Van Dijk 1971, Broadbend and Bradford 1952).

We investigated the adsorption capacity of peat with three methods:

1. A solution containing a mixture of several metals was shaken with varying amounts of peat.
2. The metal solution was allowed to flow though a column containing a constant amount of peat.
3. The metal solution was shaken with the constant a mount of peat as used in the peat column.

We used two types of milled peat. The first was from the Rastunsuo peat production area, type CS and the degree of humification was H 6—7 in von Post's scale. The other was from Jouttenisenneva peat production area, type SC and the degree of humification was H 5—6. Peat was used as received, only the biggest inhomogenities were removed, i.e. pieces of trees etc. We chose relatively well humified peats since their composition is quite homogenous. Different peat types were used to obtain the deviation in quality.

The experiments were performed in the following way:

1. To a vessel of volume 500 cm³, 2—25 g of moist peat and 100 cm³ of solution containing eight different metal ions were introduced. The pH-value of the metal solution was 2.95. The contents of the metals were chosen according to their sensitivity of determination and they were expressed as µg/cm³: Cd^{2+} =

Table 1. Results of the shaking experiments of metal ions in the mixture of metal ions.

Taulukko 1. Ravistelukokeiden tulokset, jotka on saatu vakiomääräisellä metalli-ionien seoksella, mutta turvemäärää on vaihdeltu. Sitoutuminen on ilmoitettu µekv/g ja kokeet on suoritettu sekä Rastunsuon että Jouttenisennevan turpeilla.

Peat from Rastunsuo — Peat from Jouttenisenneva

Metal ion	Added metal µg	Peat from Rastunsuo Dry weight of the sample g	Bound µg	Binding percentage	µ eqv/g	Peat from Jouttenisenneva Dry weight of the sample g	Bound µg	Binding percentage	µeqv/g
Cu^{2+}	250	11.44	230	92.2	0.63	4.931	250	100	1.60
”	250	7.668	227	91.0	0.93	2.853	247.9	99.2	2.73
”	250	2.354	233	93.2	3.12	1.804	244.9	98.0	4.27
”	250	1.296	232	92.8	5.63	0.867	225.4	90.2	8.18
”	250	0.642	222	89.0	10.9	0.477	184.5	73.8	12.2
Pb^{2+}	400	11.44	400	100	0.34	4.931	400	100	0.78
”	400	7.668	400	100	0.50	2.853	400	100	1.35
”	400	2.354	400	100	1.64	1.804	400	100	2.14
”	400	1.296	400	100	2.98	0.867	383.5	95.9	4.27
”	400	0.642	400	100	6.01	0.477	355.3	88.8	7.19
Cd^{2+}	50	11.44	50.0	100	0.08	4.91	47.3	94.6	0.17
”	50	7.668	50.0	100	0.12	2.853	43.3	86.5	0.27
”	50	2.354	48.2	96.4	0.36	1.804	38.7	77.4	0.38
”	50	1.296	43.2	86.4	0.59	0.867	21.9	43.8	0.45
”	50	0.642	29.3	58.6	0.81	0.477	9.3	18.6	0.35
Co^{2+}	250	11.44	250	100	0.74	4.931	224.2	89.7	1.54
”	250	7.668	250	100	1.11	2.853	198.2	79.3	2.36
”	250	2.354	232.7	93.1	3.35	1.804	159.3	63.7	3.00
”	250	1.296	192.0	76.8	5.03	0.867	73.5	29.4	2.88
”	250	0.642	104.0	41.6	5.50	0.477	31.2	12.5	2.22
Ni^{2+}	250	11.44	239.5	95.8	0.71	4.931	239.9	96.0	1.66
”	250	7.668	238.3	95.3	1.06	2.853	219.7	87.9	2.62
”	250	2.354	228.3	91.3	3.30	1.804	198.8	79.5	3.75
”	250	1.296	208.3	83.3	5.47	0.867	113.8	45.5	4.47
”	250	0.642	138.0	55.2	7.32	0.477	65.8	26.3	4.70
Zn^{2+}	100	11.44	92.6	92.6	0.25	4.931	83.9	83.9	0.52
”	100	7.668	90.0	90.0	0.36	2.853	70.6	70.6	0.76
”	100	2.354	82.0	82.0	1.07	1.804	57.3	57.3	0.97
”	100	1.296	71.7	71.7	1.69	0.867	23.0	23.0	0.81
”	100	0.642	38.0	38.0	1.81	0.477	2.7	2.7	0.17
Mn^{2+}	100	11.44	70.9	70.9	0.23	4.931	—	—	—
”	100	7.668	81.4	81.4	0.39	2.853	—	—	—
”	100	2.354	60.9	60.9	0.94	1.804	—	—	—
”	100	1.296	36.6	36.6	1.03	0.867	—	—	—
”	100	0.642	0.0	0.0	0	0.477	—	—	—

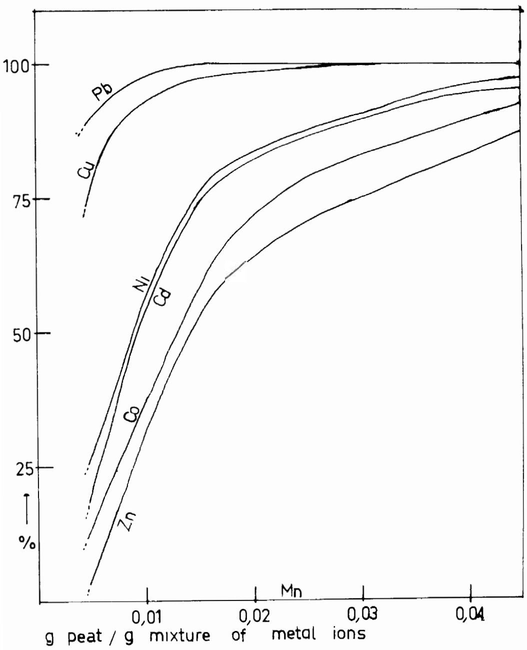

Fig. 1. The adsorption capacity of metal ions on the Jouttenisenneva peat expressed as percentages from the mixture of metal ions after the shaking experiments.

Kuva 1. Metalli-ionien adsorptiokapasiteetit prosentteina Jouttenisennevan turpeelle. Tulokset on saatu ravistelukokeilla, joissa turvemäärän ja vakio koostumuksen omaavan metalli-ionien liuoksen määrän suhdetta on vaihdeltu.

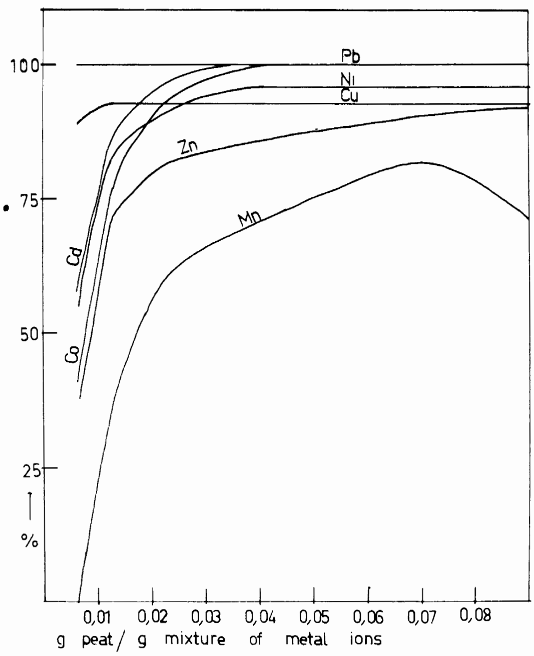

Fig. 2. The adsorption capacity of metal ion on the Rastunsuo peat expressed as percentages from the mixture of metal ions after the shaking experiments.

Kuva 2. Metalli-ionien adsorptiokapasiteetit prosentteina Rastunsuon turpeelle. Tulokset on saatu ravistelukokeilla, joissa turvemäärän ja vakio koostumuksen omaavan metalli-ionien liuoksen määrän suhdetta on vaihdeltu.

0.50, $Cu^{2+}=2.50$, $Ni^{2+}=2.50$, $Co^{2+}=2.50$, $Pb^{2+}=4.00$, $Zn^{2+}=1.00$, $Mn^{2+}=1.00$. The vessels were placed into the shaking device, and the total shaking time was 22 hours. Following this, the samples were filtered and the metals were determined from the filtrates.

2. The column tests were performed using a chromatographic column, the diameter of which was 2 cm and length 50 cm. Exactly 4.55—4.60 g of peat with known moisture was transferred to the column. The height of peat in the column was 5.0 cm and its volume was 16 cm³. The peat column was carefully moistened before use and the air bubbles were removed with suction. The solution to be investigated was poured to the column with the height of the solution being kept at a minimum level of 25 cm. During the experiments, the dropping velocity was adjusted constantly by 1.5 ml per minute. The volume of one fraction flowing through the column was 25 ml and the metal contents were determined thereafter.
3. The adsorption of a single metal was also investigated shaking 16 cm³ of peat with the same amount of metal as used in the column experiments. The other conditions were as described in section 1. In sections 2 and 3 the concentrations (in ppm) and pH-values (in parenthesis) were as follows: $Cd^{2+}=100$ (3.3), $Cu^{2+}=100$ (3.0), $Ni^{2+}=50$ (3.4), $Co^{2+}=50$ (3.4), $Pb^{2+}=200$ (2.9), $Zn^{2+}=50$ (3.3) and $Mn^{2+}=50$ (3.3). The pH-values of solutions were adjusted relatively low to prevent the formation of hydroxides. The metal contents were determined with an atomic absorption spectrophotometer (Southern Analytical A 3000) and the sensitivities of determinations were in agreement with the literature values.

The concentrations of stock solutions were 1000 ppm, with the exception of Pb^{2+}, whose concentration was 20000 ppm. The stock solution were prepared from pro analysi reagents (E. Merck AG and Baker Ltd). The concentrations of stock solutions were determined under known methods.

Table 1. shows the results from the shaking experiment. The peat originating from Rastunsuo has better adsorption capacity than the peat from Jouttenisenneva. The metals adsorbed by the peat from Jouttenisenneva expressed as percentages from the corresponding values of Rastunsuo peat are as follows: $Cu^{2+} = 93$ %, $Pb^{2+} = 98$ %, $Cd^{2+} = 62$ %, $Co^{2+} = 57$ %, $Ni^{2+} = 73$ % and $Zn^{2+} = 50$ %. The results have been calculated from the mixture ratio: g of peat/g of mixture = 0.01. In the case of Rastunsuo peat the mixture caused Pb^{2+} to remain totally absorbed. Figures 1 and 2 show the adsorption of metals expressed as percentages from the g of peat/g of mixture. The different adsorptions of metals can clearly be seen as well as the difference between the two peat types.

It can be seen from these experimental conditions that peat from Rastunsuo totally adsorbs lead, cadmium and cobalt. Nickel and copper are not completely adsorbed, but constantly remain to the level of 96 % and 93 %, respectively, whilst zinc is considerably less adsorbed and doesn't stabilize in these conditions. The behaviour of manganese is very exceptional. Not only is it very weakly adsorbed but it has a maximum limit. (Fig. 2). This is explained by the manganese dissolved from the peat itself.

The peat from Jouttenisenneva totally adsorbs lead and copper, but the other metals do not reach the equilibrium in these conditions. Manganese was dissolved from the peat in this case to such an extent that it showed an increased concentration, and the adsorption could not be measured (Table 1.). The order of the adsorption with both peats was as follows: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+}$ $Zn^{2+} > Mn^{2+}$.

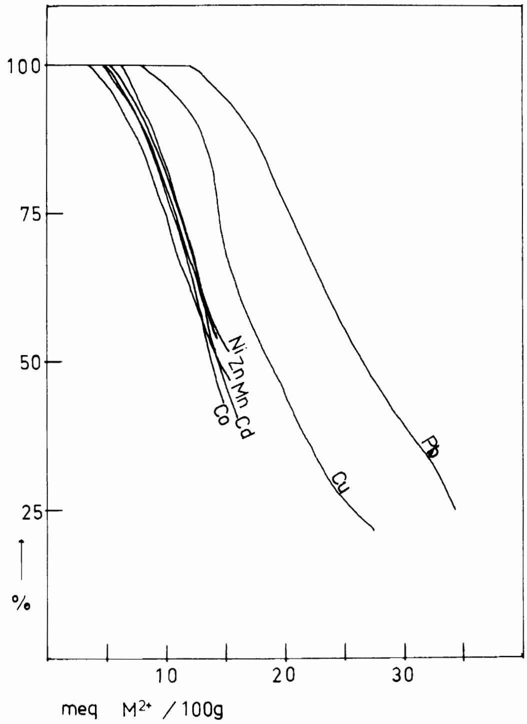

Fig. 3. The adsorption capacity of single metal ions on the Rastunsuo peat expressed as percentages from the corresponding metal ion solution in the column ion-exchange experiments.

Kuva 3. Yksittäisten metalli-ionien adsorptiokapasiteetti Rastunsuon turpeelle. Tulokset on saatu pylväsioninvaihtokokeilla ja yhden metalli-ionin käsittävillä liuoksilla. Valutusnopeus on ollut jokaisessa kokeessa sama 1,5 ml min⁻¹ ja turvemäärä on ollut vakio noin 4,5 g kuivapainoltaan.

Figure 3 shows the results from the column experiment (method 2) with Rastunsuo peat. The strongest adsorption is shown by lead and the total order of adsorption is as follows: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} \sim Mn^{2+} \sim Cd^{2+} \sim Co^{2+}$. Pb^{2+} and Cu^{2+} ions are strongly adsorbed while the mutual differences between the other metals are significantly smaller.

Table 2 shows the results from the shaking experiments (method 3). The similarity of the adsorption order with the column experiment can be noted.

Table 2. Results of the shaking experiments of the peat from Rastunsuo.

Taulukko 2. Ravistelukokeiden tulokset, jotka on saatu yksittäiselle metalli-ionille. Kokeisiin käytetty turve on ollut Rastunsuolta.

Metal	Dry weight of the sample	Added amount of metal ion	Found amount of metal ion	Amount of metal ion in peat		Capacity	
	g	ppm	ppm	ppm	$\mu g \times 10^{-3}$	mg/g	$\mu eq/g \times 10^{-1}$
Mn^{2+}	2.657	49.53	19.50	30.03	6.063	2.282	8.307
ZN^{2+}	2.657	49.53	14.25	35.28	7.123	2.681	8.203
Co^{2+}	2.675	49.53	25.20	24.33	4.912	1.836	6.231
Ni^{2+}	2.669	49.53	17.80	31.73	6.406	2.400	8.175
Cu^{2+}	2.657	99.06	32.00	67.06	13.539	5.096	16.039
Cd^{2+}	2.657	99.06	32.50	66.56	13.438	5.058	9.000
Pb^{2+}	2.657	198.09	47.60	151.3	53.24	20.038	19.342

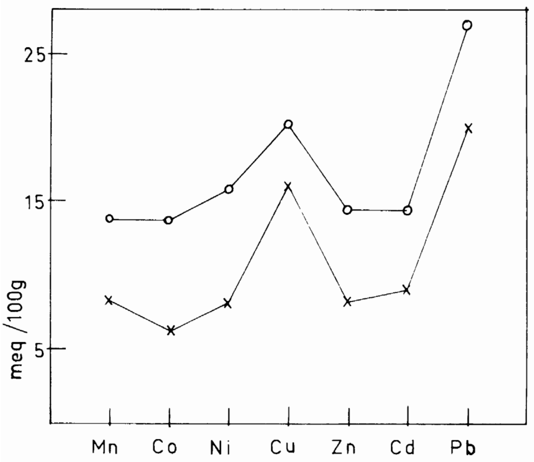

Fig. 4. The values of ion-exchange capacities from the shaking (x) and column (o) experiments for different metal ions expressed as meq/100 g of dry peat.

Kuva 4. Ioninvaihtokapasiteetin arvot, jotka on saatu ravistelukokeilla (X) tai pylväsioninvaihtokokeilla (0) eri metalli-ioneilla. Tulokset on ilmoitettu mekv/100 g kuivaa turvetta.

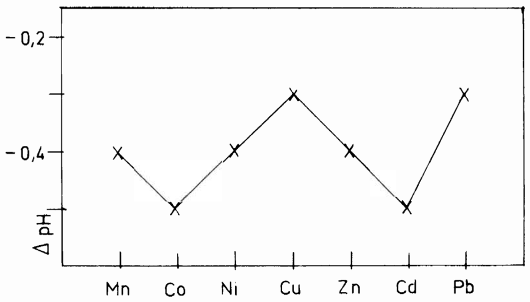

Fig. 5. The change in the proton content of the solution during the shaking experiment.

Kuva 5. Liuoksen pH:n muuttuminen ravistelukokeissa eri metalli-ioneilla.

Table 3 shows the results obtained by different methods. Methods 2 and 3 are comparable since only one ion at a time was investigated leading to the same ion activities in dilute solutions. The column chromatography proved to be a very efficient tool especially when applied to peat, as can be seen in the Figure 4. This depicts the capacities obtained from the shaking and column experiments.

Figure 5 shows the change in the proton content of the metal by metal solutions during the shaking experiments. This allows us to calculate the ion-exchange capacity, more accurate results, however, are obtained by determining the total metal contents. This difference is clearly observed when Figures 4 and 5 are compared.

The shaking of the metal mixture solutions shows that the relative amounts adsorbed obey the same order as that obtained with single ion experiments, the total adsorption capacity of peat, however, is weakened due to the changes in the ion activities which in turn are related to the total strength of the solution.

All the metal ions now under investigation are divalent with most of them having almost the same ionic radius (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; 0.72—0.78 Å), but different ionexchange capability. This implies that peat possesses strong complexing agents which dominate the ion-exchange capabilities of the metals enlisted. This assumption supported by Fig 4 where the adsorption order is seen to obey the well-known Irwing-Williams stability of metal complexes as determined with several ligands (Irwing, Williams 1948).

Since we are now dealing with the complexes of weak acids (mainly originat-

Table 3. Ion exchange capacities of Rastunsuo peat as determined by different methods.

Taulukko 3. Eri menetelmillä saadut Rastunsuon turpeen ioninvaihtokapasiteetin arvot.

	method 2		method 1						method 3	
	$\mu g/g \times 10^{-3}$	$\mu eq/g \times 10^{-1}$	$\mu g/g \times 10^{-3}$	$\mu eq/g \times 10^{-1}$	$\mu g/g \times 10^{-3}$	$\mu g/g \times 10^{-1}$	$\mu g/g \times 10^{-3}$	$\mu eq/g \times 10^{-1}$	$\mu g/g \times 10^{-3}$	$\mu eq/g \times 10^{-1}$
	1	1	2	2	3	3	2	2	2	2
Cu^{2+}	2.5	7.9	6.4	20.2	0.019[4]	0.6[4]	(>) 0.08	(>)0.28	5.1	16.0
Pb^{2+}	12.0	11.6	27.9	27.0	>0.062	>0.6	> 0.15	> 0.15	19.3	20.0
Cd^{2+}	3.5	6.2	8.1	14.3	0.001	0.02	0.02	0.03	5.1	9.0
Co^{2+}	1.3	4.4	4.0	13.6	0.005	0.2	0.09	0.29	1.8	6.2
Ni^{2+}	1.4	4.8	4.6	15.7	0.006[4]	0.2[4]	0.09	0.30	2.4	8.2
Zn^{2+}	1.4	4.3	4.7	14.4	<0.008	0.02	0.03	0.09	2.7	8.2
Mn^{2+}	0.9	3.3	3.9	13.7	0.000	0.00	0.02	0.07	2.3	8.3

1. Binding percentage >99.5 %
2. Total capacity
3. The capacity at the point in which the minimum amount of peat binds more than 99.5 % of the metal ions.
4. After reaching the constant binding level (90—<100 %)

ing from humus substances) the pH has a great influence on the adsorption. This is illustrated by the cadmium adsorption in Fig. 6, and thus one reason why pH must always be taken into account when comparing values from different methods.

As mentioned earlier, our results are not easily comparable with other investigations since there are variations in both the methods used and pretreatment of the sample. Unlike others we used milled peat as recieved from production and did not convert it to proton form. In this way it was thought a better distinction between the different peat types would be possible.

Figure 4 shows the ion-exchange capacities (in meg/100 g of dry material) for the Rastunsuo peat. Belkevich et al. have obtained the following values for the ion affinity order at pH 6.0—6.2: $Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$ (Belkevich et al. 1972 (a)) and $Zn^{2+} < Mn^{2+} < H^{+} < Cu^{2+}$ (Belkevich et al. 1972(b)). On the whole the figures prove to be consistent with our results concerning the order of ions, Jouttenisenneva however, makes an exception with manganese.

One of the most comprehensive kinetic studies incorporating several metals has been performed by Bunzl et al. (Bunzl et al. 1976). They report the capacity order of ions as the following: $Pb^{2+} > Cu^{2+} > Cd^{2+} \sim Zn^{2+} > Ca^{2+}$. We are able to confirm the same order but observe considerably larger differences between lead and copper ions and between copper and the other ions.

A quantitative comparison is also very difficult, for instance, the ion-exchange capacity of copper has been reported as being 317 meq/100 g (Belkevich et al. 1976) and 74 meq/100 g (Sapek, 1976), whereas our column experiments resulted in 20 meq/100 g and the shaking experiments 16 meq/100 g. As far as the lead ion is concerned 133 meq/100 g has been reported (Bunzl et al. 1976), as opposed to our valves of 27 and 20 meq/100 g respectively. The values reported by Belkevich and Bunzl concerning the adsorption of lead and copper are in mutual disagreement.

SUMMARY

The basic problem in investigating the ion-exchange properties of peat is the pretreatment of peat sample and the selection of the methods used. Together these render the comparison of the results very difficult. We decided to use unpretreated peat with our measuring method based on the determination of metal ion contents. We observed that the determination of metal ion contents gave more accurate results than those methods based on the pH determinations. The latter is distorted by the fluctuations in the ionic strength, a discrepancy which cannot be eliminated without uncertainty.

The adsorption of the ions by the peat obeyed the Irwing-Williams order of complex formation. For this reason peat can be referred to as a chelating ion-exchanger. This property makes this ion-exchanger very sensitive to the pH, which is reflected in the derivative results reported by several authors regarding the ion-exchange capacity.

The peats under investigation were of different origins and showed significant differences in the ion-exchange capacity. We conclude therefore, that the peat bog and peat itself are the important factors determining the ion-exchange properties, especially in those peats which undergo strong humification processes.

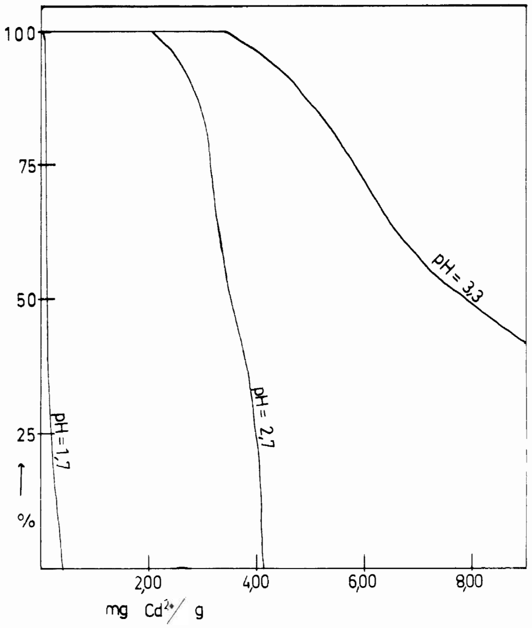

Fig. 6. The influence of pH on the adsorption of cadmium in the column experiment.

Kuva 6. pH:n vaikutus kadmiumin adsorptioon.

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SELOSTE:

TURPEEN IONINVAIHTO-OMINAISUUKSISTA

OSA I: ERÄIDEN 2-ARVOISTEN METALLI-IONIEN ADSORPTIO TURPEESEEN

Turpeen ioninvaihto-ominaisuuksia tutkittaessa kohdataan heti aluksi kaksi vaikeutta: 1) tutkimusmenetelmän valinta, 2) turpeen esikäsittely tutkimuksia varten.

Valitsimme tutkimusmenetelmiksi staattisen ravistelumenetelmän, jossa tunnettua määrää turvetta ravisteltiin metalliliuoksella kunnes oli saavutettu tasapainotila. Tämän jälkeen liuoksen metallipitoisuus määritettiin ja sen muutoksesta alkuperäisen liuospitoisuuden nähden voitiin laskea turpeeseen sitoutuneen metalli-ioninmäärän. Toiseksi menetelmäksi valitsimme dynaamisen menetelmän, jossa tunnetun turvemäärän läpi valutetaan vakionopeudella vakiopitoista metalli-ionin liuosta. Liuoksen konsentraation muutoksesta voidaan laskea turpeen sitoma metalli-ionien määrä. Kuten kuvasta 4 selviää, niin pylväskokeilla saadaan suuremmat ioninvaihtokapasiteetin arvot kuin ravistelukokeilla. Kokeisiin käytimme sellaisenaan jyrsinturvetta.

Eri ionien adsorptiojärjestys noudattaa Irwing-Williams'in siirtymäalkuainemetallien kompleksinmuodostusjärjestystä (Kuva 4 ja 5). Tämä on osoituksena, että lähinnä kemiallisten sidosten muodostus turpeen komponenttien ja metalli-ionien välillä hallitsee ionien adsorptiota, josta syystä ioninvaihtokapasiteetin arvo on myös voimakkaasti pH:sta riippuvainen (Kuva 6).

Ei ainoastaan turvetyyppi, vaan myös suon sijainti vaikuttaa turpeen ionienvaihto-ominaisuuksiin.

Kun verrataan eri tutkijoiden saamia tuloksia keskenään, niin on muistettava, että tutkimustulokset riippuvat suuresti käytetystä tutkimusmenetelmästä ja turpeen esikäsittelystä.