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# ON THE ION-EXCHANGE PROPERTIES OF PEAT

## PART II:

## ON THE ADSORPTION OF ALKALI, EARTH ALKALI, ALUMINIUM (III), CHROMIUM (III), IRON (III), SILVER, MERCURY (II) AND AMMONIUM IONS TO THE PEAT

## TURPEEN IONINVAIHTO-OMINAISUUKSISTA
## OSA II: ERÄIDEN METALLI-IONIEN ADSORPTIO TURPEESEEN

In the previous part of our work we investigated the ion-exchange capacities of heavy metals on the peat and simultaneously, the influence of different research methods on the results. The ability of form bindings with the chelating agents existing in peat mostly affects on the adsorption of heavy metals to this material (Tummavuori and Aho 1980).

In this article we have investigated the adsorption of alkali, earth alkali, aluminium (III), chromium (III), iron (III), silver, mercury (II) and ammonium ions to the peat. Furthermore, we have used the same milled peat from Rastunsuo as in previous part.

The stock solution were prepared from analytically pure nitrates or chlorides (except aluminium from its sulphate) of the metals. The reagents were products of either E. Merck AG or T. Baker Ltd. The concentrations of stock solutions were 1000 ppm except chromium, which was 0.1 M. The pH-value of the solutions used in the experiments was adjusted to 3.3 with nitric acid. The concentrations of the solutions used in experiments are presented in Table 1.

We started with shaking experiments, where the known amount of peat was shaken with metal solution of known content for about 20 hours (see Table 1.).

The other approach was the column method, where the metal solution was allowed to flow though a peat column, 16 cm$^3$ by its volume, with constant velocity. More detailed description of the experimental arrangements can be found in the previous article (Tummavuori and Aho, 1979).

The contents of sodium, potassium, lithium, barium and strontium were determined with flame emission (EEL-flame photometer and atomic absorption spectrophotometer in emission mode). Magnesium, calcium, chromium (III) and mercury (II) with atomic absorption (A 3000 Southern Analytical and Perkin — Elmer 5000).

Iron (III), aluminium (III) and ammonium ions were determined colorimetrically with Pge Unicam spectrophotometer (Sandell 1959, Hammet et al. 1925, Geiger 1942). The content of silver ions was determined with potentiometric titration using potassium iodide (Kolthoff et al. 1936).

The results of the shaking experiments are collected in Table 1 and Figs. 1—3 depict the results from the column experiments. Figs. 2 and 3 show the percent of adsorption from the total content of metal ion flowed through the column as a function of the amount of metal equivalent. The figures show, how different metals saturate peat with different speeds. Potassium, barium, sodium and calcium ions saturate the column very rapidly. The tri-

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Table 1. The values of ion-exchange capacities of different metal ions obtained form the shaking experiments

*Taulukko 1. Metalli-ionien ioninvaihtokapasiteetin arvot, jotka on saatu staattisella ravistelumenetelmällä.*

| Metal | Wet weight of the sample g | Dry weight of the sample g | Added amount of metal ion ppm | Found amount of metal ion ppm | Amount of metal ion in peat | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | ppm | mg | mg/g | eq/g × $10^{-1}$ |
| $Li^+$ | 4.55 | 2.657 | 49.1 | 46.0 | 3.1 | 0.316 | 0.12 | 1.7 |
| $Na^+$ | 4.60 | 2.686 | 49.1 | 33.0 | 16.1 | 1.641 | 0.61 | 2.7 |
| $K^+$ | 4.55 | 2.657 | 49.1 | 31.1 | 18.0 | 1.834 | 0.69 | 1.8 |
| $Mg^{2+}$ | 4.55 | 2.657 | 49.1 | 31.3 | 17.8 | 1.814 | 0.68 | 5.6 |
| $Ca^{2+}$ | 4.55 | 2.657 | 49.1 | 23.5 | 25.6 | 2.609 | 0.98 | 4.9 |
| $Sr^{2+}$ | 4.56 | 2.663 | 248 | 157 | 91 | 18.37 | 6.9 | 15.8 |
| $Ba^{2+}$ | 4.55 | 2.657 | 49.1 | 13.0 | 36.1 | 3.678 | 1.4 | 2.0 |
| $Hg^{2+}$ | 4.56 | 2.663 | 297 | 207 | 90 | 18.17 | 6.8 | 6.8 |
| $Ag^+$ | 4.58 | 2.675 | 99.1 | 25.9 | 73.2 | 14.78 | 5.5 | 5.1 |
| $Fe^{3+}$ | 4.55 | 2.657 | 297 | 203 | 94 | 18.98 | 7.1 | 38.4 |
| $Al^{3+}$ | 4.55 | 2.657 | 99.1 | 95.2 | 3.9 | 0.787 | 0.30 | 3.3 |
| $Cr^{3+}$ | 4.55 | 2.657 | 105.0 | 44.6 | 60.4 | 12.20 | 4.6 | 26.5 |

valent metal ions reach the saturation equilibrium very slowly.

The values of the ion-exchange capacities can be obtained with column experiments as shown by Figs. 1 and 2. The minimum amount of metal ions, which is adsorbed by the column can be estimated. This amount is described by the area remaining inside the axes and the curve. The accuracy of the method was tested by eluating the adsorbed metal ions out of the column with acid and by determining the content of the metal ions released by the column. The results were in good agreement with those obtained from the area calculations.

Fig. 3 shows the values of the exchange capacities of ions as obtained from the shaking and column experiments in units of meq/100 g of dry peat.

The column experiments usually give larger values. The differences are significantly larger in case of lithium, magnesium and aluminium (III) ions.

The adsorption order of monovalent alkali metals given by the column experiments was $Li^+ \gg Na^+ \approx K^+$ and $Li^+ < Na^+ \approx K^+$ with shaking experiments. The weak adsorption of lithium, having a small ionic radius, in shaking experiments is noteworth. (Also the experiments with different concentrations gave similar results).

In previous works the ion-exchange capacity of sodium and potassium ions has been reported to be rather small where as lithium has larger capacity than those. (Virri 1976, Belkevich 1976).

For the capacity order of divalent earth alkali metals, we obtained $Sr^{2+} \gg Mg^{2+} > Ca^{2+} > Ba^{2+}$.

The strontium ion makes a noticeable exception from the others. This shows that the peat we have experienced possesses a component specific for strontium. We have not isolated this component, yet. If we neglect strontium ion in this particular case, the order principally corresponds to the order presented in the literature, but the

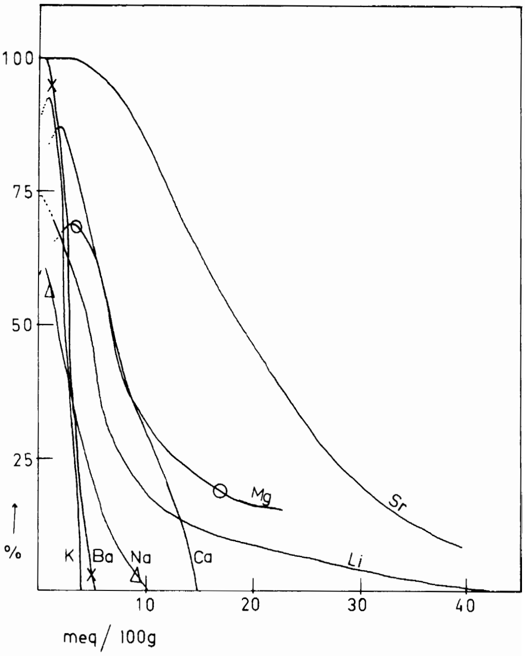

Figure 1. The adsorption of alkali and earth alkali metal ions as percentages from the solution of the metal ions in the shaking experiments.

*Kuva 1. Alkali- ja maa-alkali-ionien adsorptio prosentteina liuoksestaan. Tulokset on saatu ravistelukokeilla.*

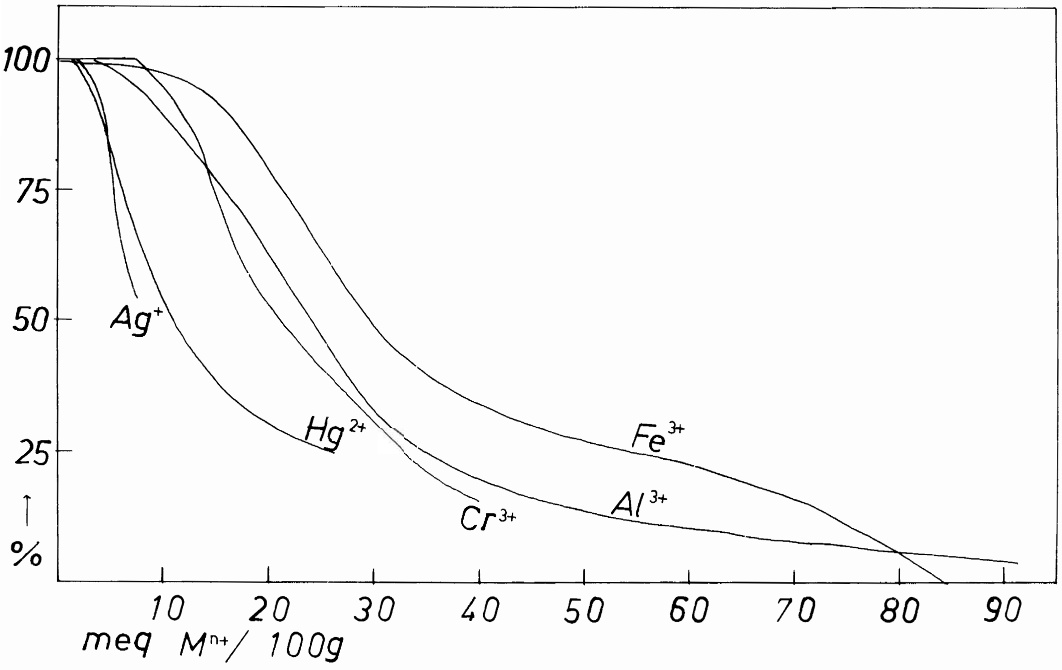

Figure 2. The adsorption of some heavy metals as percentages from the solution of the metal ions in the shaking experiments.

*Kuva 2. Eräiden raskaiden metalli-ionien adsorptio prosentteina liuoksestaan. Tulokset on saatu ravistelukokeilla.*

quantitative judgement of the results is not reasonable due to the large deviation (Belkevich 1976, Ratschak and Jungk 1964, Jungk 1964).

The mutual order of aluminium (III), chromium (III) and iron (III) in shaking experiments obeyed the common complex formation order given to these ions. Since the pH value of the solutions was slightly above 3, the formation of hydroxides and hydroxide complexes with these metals is possible and leads to the deviations in the results.

Aluminium (III) is considerably more adsorbed in the column than in the shaking experiments. This is due to the reason, that in the dynamic conditions of the column the hydrolysis of the aluminium ion has no time to take place.

In the shaking experiments, the partial precipitation of the iron (III) has occured which explains the larger values in the exchange capacity than in the column experiments with these concentrations.

The investigations of the exchange capacities of these trivalent ions has gained only minor attention due to the reason that the experiments must be performed at rather low pH, but the impression of Puustjärvi concerning to the strong adsorption of these ions to the peat is well justified (Puustjärvi 1961).

The adsorption of silver ion is about the same order of magnitude as with magnesium ion. This illustrates the relatively stronger ability of the complex formation of silver as compared with magnesium which has a stronger surface charge.

The adsorption of mercury (II) ion in

Table 2. The values of ion-exchange capacities of different metal ions obtained from the column experiments.

*Taulukko 2. Metalli-ionien ioninvaihtokapasiteetin arvot, jotka on määritetty dynaamisilla pylväskokeilla. Taulukossa on ilmoitettu kapasiteetin arvot ilman metalli-ionin läpipäästöä ja kokonaiskapasiteetti.*

| Ion | The capacity without leakage | | The whole capacity | |
|---|---|---|---|---|
| | mg/g | ueq/g × 10⁻¹ | mg/g | ueq/g × 10⁻¹ |
| $NH_2^+$ | 0.0 | 0.0 | 0 | 0 |
| Li* | 0.0 | 0.0 | 0.48 | 7.0 |
| $Na^+$ | 0.0 | 0.0 | 0.54 | 2.3 |
| $K^+$ | 0.0 | 0.0 | 0.93 | 2.3 |
| $Mg^{2+}$ | 0.0 | 0.0 | 1.19 | 9.7 |
| $Ca^{2+}$ | 0.0 | 0.0 | 1.35 | 6.7 |
| $Sr^{2+}$ | | | 9.08 | 20.7 |
| $Ba^{2+}$ | 0.03 | 0.05 | 1.81 | 2.6 |
| $Al^{3+}$ | 0.27 | 3.0 | 2.77 | 30.8 |
| $Fe^{3+}$ | ~ 0.8 | ~ 3 | 6.55 | 35.2 |
| $Cr^{3+}$ | 1.3 | 7.3 | 4.62 | 26.6 |
| $Ag^+$ | 2.2 | 2.0 | 7.23 | 7.8 |
| $Hg^{2+}$ | 1.5 | 1.5 | 16.3 | 16.2 |

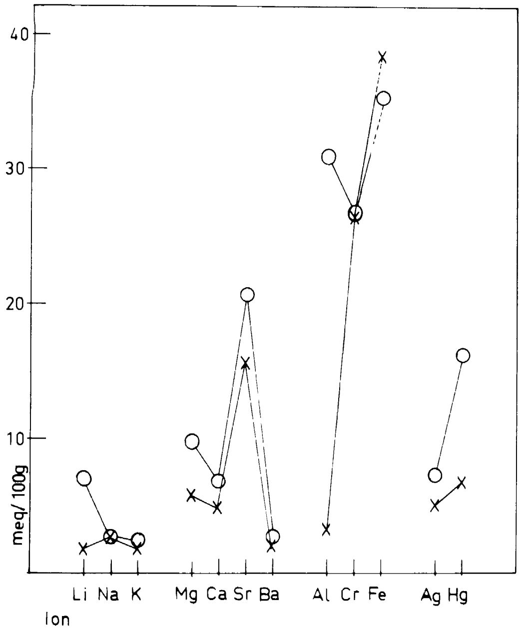

Figure 3. The values of ion-exchange capacities of different metal ions in meq/100 g after shaking (X) and column (0) experiments.

*Kuva 3. Metalli-ionien ioninvaihtokapasiteetin arvot mekv/100 g kuivaa turvetta. Ravistelukokeilla saadut tulokset on merkitty (X) ja pylväskokeilla saadut (0).*

the shaking experiments remained at the same level as with silver ion, but showed a markedly stronger adsorption in the column experiments. The difference is due to the side reactions occurring in the static conditions of the shaking experiments.

On the opposite to the literature data, we did not observe the adsorption of ammonium ion to the peat in our experiments, although if should be adsorbed as much as reported for potassium (Jungk 1964, von Ratschak and Jungk 1964).

Thanks to the relatively good adsorption capacity of peat, some attempts have been made use it in technical applications.

To increase the adsorption capacity of peat it can be oxidized or some reagents can be added (Belkevich 1976, Lalancette 1972, Wilhelms, 1973).

Along with the oil price, the prices of reagents and ion-exchange resins will strongly increase. This suggests, that the possibilites of untreated peat as ion-exchange "resin" are worth of further investigations (Brown 1976).

For example, one ton of untreated peat adsorbs totally about 12 kg of lead, which easily can be released from the peat by treatment with dilute acid solutions.

## SUMMARY

In the shaking experiments in case of the alkali metals and peat, the ionic radii of the ions have no influence on the adsorption. The alkali earth metals obey the suggested order of adsorption which depends on the ionic radius. The exception showed by strontium ion only confirms our impression of the variable features of different peat types. It is obvious, however, that the adsorption of strontium in averge conditions obeys the same order as the others do and is dependent on the ionic radius. We carry on the investigations with this particular matter.

The results obtained from the adsorption of heavy metals in this study are directive, but show that in favorable circumstances these metals are quite considerably adsorbed by peat types. It is obvious, however, that the adsorption of strontium in averge conditions obeys the same order as the others do and is dependent on the ionic radius. We carry on the investigations with this particular matter.

The results obtained from the adsorption of heavy metals in this study are directive, but show that in favorable circumstances these metals are quite considerably adsorbed by peat. The most important factor on the adsorption within these metals in the pH of the solution. A very surprising fact was the behaviour of ammonium ion, since it was not adsorbed by the untreated peat we used. As could be expected, we did not observe the adsorption of any anions.

Because peat still is quite a cheap material and possesses a relatively good adsorption capacity, the further studies for the development of peat — based, large ion — exchangers e.g. for industrial purposes are of interest. One good application might be the purification of waste waters by removing the harmful cations before the waters are allowed to go to the municipal drainage system.

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## LYHENNELMÄ:

# TURPEEN IONINVAIHTO-OMINAISUUKSISTA
# OSA II: ERÄIDEN METALLI-IONIEN ADSORPTIO TURPEESEEN

Turpeen ioninvaihtotutkimuksiemme tässä osassa olemme tutkineet alkaali-, maa-alkaali-, eräiden kolmenarvoisten metallien, hopea-, elohopea(II)- ja ammoniumionien, adsorpoitumista turpeeseen.

Alkali- ja maa-alkalimetalli-ionit noudattavat ionsäteittensä mukaista odotettua sitoutumista eli että pienemmän ionisäteen omaava ioni sitoutuu voimakkaimmin. Ainoan poikkeuksen tekee stronttiumioni, jonka sitoutuminen on poikkeuksellisen voimakasta. Pyrimme selvittämään jatkossa syyn stronttiumin voimakkaaseen kelatoitumiseen. Myöskin ammoniumioni on poikkeava, sillä se ei absorpoidu lainkaan turpeeseen näissä tutkimusolosuhteissa.

Kolmiarvoisten raskaiden metalli-ionien tutkimuksiin vaikuttavat jo niiden taipumus muodostaa hydroksideja. Tämä aiheuttaa tuloksissa huomattavaa hajontaa, mikä voidaan todeta kuvasta 3.

Elohopea(II)-ioni absorpoituu pylväskokeissa huomattavan voimakkaasti, mutta staattisissa ravistelukokeissa heikohkosti. Tämä johtunee elohopean hydroksidien muodostuksesta.

Koska turve on yhä halpa materiaali ja öljypohjaisten ioninvaihtohartsien hinta kohoaa jatkuvasti, niin on syytä jatkaa turpeen ioninvaihto-ominaisuuksien tutkimuksia. Tulevien tutkimusten tarkoituksena on selvittää niitä tekijöitä, jotka vaikuttavat eniten ioninvaihto-ominaisuuksiin, jotta löytäisimme keinot parantaa turpeen ioninvaihtokapasiteettia ja mahdollisesti saada käyttökelpoinen vaihtoehto nykyisille ioninvaihtohartseille.