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Simultaneous adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} on peat

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TABLE OF CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers which have been re-printed with the permission of the publishers.

   I. **Ü. Sõukand**, R.Tungel, T.Tenno. Comparison of heavy metals adsorption properties on natural and granulated peat on example of cadmium, Proceedings of the Estonian Academy of Sciences. Chemistry, 1996, 45, 123–129

  II. M. Kaasik, **Ü. Sõukand**. Balance of alkaline and acidic air pollution loads in the area affected by oil shale combustion, Oil Shale, 2000, 17, 113–128

 III. M. Kaasik, R. Rõõm, O. Royset, **Ü. Sõukand**, M. Vatset, K. Tõugu. Elemental and base anions deposition in the snow cover of North Eastern Estonia. Water, Air, and Soil Pollution, 2000, 121, 349–366

 IV. **Ü. Sõukand**, R. Sõukand, A. Maširin, T.Tenno. The Langmuir two-surface equation as a model for cadmium adsorption on peat: A new method of calculation of equation constants. Environmental Science and Pollution Research International, Special Issue 1, 2002, 43–48

  V. **Ü. Sõukand**, P. Kängsepp, R. Kakum, T. Tenno, L. Mathiasson, W. Hogland. Selection of adsorbents for treatment of leachate: batch studies of simultaneous adsorption of heavy metals. Journal of Material Cycles and Waste Management, 2010, 12, 57–65

Contribution by the author to the different papers
   I. The author was fully responsible for the outlining of the experimental strategy, performed a major part of the experiments, was engaged in scientific discussions and wrote the major part of the paper.
  II. The author was engaged in planning the experimental strategy, performed a substantial part of the experiments and sampling in the field and contributed actively to scientific discussions and writing of the paper.
 III. The author was engaged in planning the experimental strategy, performed a substantial part of the experiments and sampling in the field and contributed actively to scientific discussions and writing of the paper.
 IV. The author was fully responsible for the outlining of the experimental strategy, performed and supervised a major part of the experiments, contributed to the development of the mathematical model, was engaged in scientific discussions and wrote the major part of the paper.
  V. The author was fully responsible for the outlining of the experimental strategy, performed and supervised a major part of the experiments, was engaged in scientific discussions and wrote the major part of the paper.

ABBREVIATIONS AND SYMBOLS

C_0	initial concentration of solution of metal
C_e	concentration of metal in solution at equilibrium
$C_{e\,i}$	concentration of metal in solution at equilibrium for the data point i
G	gauss
ICP-AES	inductively coupled plasma atomic emission spectrometer
ICP-MS	inductively coupled plasma mass spectrometer
K_L	adsorption equilibrium constant
K_{L1}	adsorption equilibrium constant for the first monolayer
K_{L2}	adsorption equilibrium constant for the second monolayer
min	minute
m	mass (dry weight) of adsorbent used
MJ	mega joule
n	number of data points
nM	nanometre
PCA	principal component method of factor analysis
PP	power plant
q_e	equilibrium solid phase concentration
$q_{e\,i}$	equilibrium solid phase concentration for the data point i
$q_{e\,i}^{\ 1}$	equilibrium solid phase concentration for the data point i, calculated with Langmuir isotherm equation
q_e %	percentage equilibrium solid phase concentration or percentage adsorption
q_m	maximum uptake capacity of the adsorbent
q_{m1}	maximum uptake capacity of the first monolayer
q_{m2}	maximum uptake capacity of the second monolayer
R^2	correlation coefficient of regression or coefficient of determination
r_i	ionic radius
r_h	hydrated radius or ionic radius of hydrated ions
R_i	relative metal adsorption (%)
rpm	rounds per minute
s	standard deviation
SW	south-west
V	volume of aqueous phase
θ_I	relative coverage

1. INTRODUCTION

1.1. Selection of the adsorbent and the adsorption of Cd^{2+}, Pb^{2+}, and Ni^{2+} from single- and multimetal solutions

Several inorganic and organic compounds such as heavy metals, fuels and petroleum industry products cause soil and water contamination. Unlike organic pollutants, heavy metals do not undergo biological degradation and tend to accumulate in organisms, thereby eventually entering the food chain [1, 2]. A great deal of industrial wastewater containing various heavy metal ions is discharged annually by a number of industries. Effluents from smelting, electrolyzing, drug manufacturing, paint preparation, alloy manufacture, galvanizing operations, printing, dyeing, paper making, ceramics manufacture and inorganic dyestuff preparation contribute to this stream [3]. Although some metals are necessary for biological processes, all of them are toxic in high concentrations. This is due to their oxidative capacity to form free radicals and their ability to replace essential metals in enzymes, interrupting their normal activity. Other metals are not essential and accumulate in different organisms and that is why they are toxic even in low concentrations [2, 4]. Cadmium (Cd), copper (Cu), lead (Pb), and nickel (Ni) belong to the group of seriously hazardous heavy metals. Due to their high toxicity various government agencies have imposed strict and more stringent environmental legislations on wastewater discharges. Removal of heavy metals from wastewater has been a subject of major concern to scientists for many years [1].

The most commonly applied physico-chemical treatment methods are: (i) precipitation as hydroxides, carbonates or sulfides and subsequent liquid-solid separation by gravity settling, and flotation or filtration, (ii) sorption (adsorption, ion exchange), (iii) membrane processes, (iv) electrolytic recovery and (v) liquid-liquid extraction. However, each method has its merits and limitations in application, and they are often limited by technical and economical issues. The adsorption process is arguably one of the more popular methods for the removal of heavy metal ions because of its simplicity, convenience, and high removal efficiency [5]. The process of adsorption implies the presence of an "adsorbent" solid that binds molecules or ions by physical attractive forces, ion exchange, and chemical binding [6].

Peat is a polar, highly porous material that can have significant applications as an adsorbent for the removal of heavy metals from aqueous solutions. Peat is a type of soil that consists mostly of organic matter and is formed under certain temperature and humidity as well as under specific aerobic and other conditions. It is a complex material with lignin, cellulose, and humic substances as its major constituents. The polar functional groups of lignin and humic fractions, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers, are involved in the formation of chemical bonds. Because of the polar character of peat, it appears to have a good potential for the adsorption of metals

[1, 7, 8]. Research by several investigators has demonstrated that peat is an effective adsorbent for the removal of heavy metals from wastewater [9–16]. The abundance of peat and its easy availability makes it an economical adsorbent [8, 17].

Many artificial adsorbents for water treatment such as ion-exchange materials and activated carbon have been developed during the past decade. Their high prices make them less suitable for wastewater treatment although they might be used as a polishing step after most of the pollutants have already been removed. However, when it comes to a large-scale treatment of waste-water, such as leachate from landfills, the adsorbents used must be inexpensive. As stated by Bailey, S. E. *et al.* [18], an adsorbent can be assumed to be cheap if it requires little processing, is abundant in nature, or is a by-product or waste material from another industrial or agricultural operation. In general, numerous types of potential sorbents are available and the mixing of adsorbents with different properties might be a good alternative for achieving the removal of different types of pollutants. However, the suitability of certain materials for the removal of pollutants needs to be clarified for each application since polluted waters such as leachate from landfills have complex compositions, containing pollutants with widely different chemical properties.

Scientific studies have demonstrated that several adsorbents are capable of removing heavy metals [13, 18–20]. For instance, metals can be removed by peat from water solutions of a single metal ion [6, 17, 18, 21, 22], as well as from water solutions containing two [8, 16, 23], three [1, 3, 24–27], four, or even more metals [15, 28, 29]. Although mixed metal solutions are used in many studies, the competitive adsorption of metals has not always been evaluated in detail [12, 24, 29]. Multimetal competitive adsorption has exten-sively been studied using various biosorbents. These include microorganisms, such as fungi [30–36], bacteria [2, 37], and algae [31, 38–41] and lignocellulose biomaterials, such as tobacco dust [42], spruce wood, pine bark, cork [43], peat moss [8, 28, 44], sheep manure [45], chitosan beads [46] etc. In addition to biosorbents, single- and multimetal adsorption studies have been carried out on adsorbents with very different properties, such as activated carbon [47, 48], goethite [49], a mineral matrix composed of tropical soils [50], cation exchange resin [51], and kaolinite [52]. Multimetal competitive adsorption onto peat has been described in only a few articles [1, 3, 8, 25, 26, 53]. For all investigations dried, grounded, and sieved peat was used.

To our knowledge it seems that there are no reports on the use of highly decomposed, non-dried and non-pre-treated peat in multimetal competitive adsorption investigations. This work investigates multimetal adsorption of three different metals onto peat the samples of which were untreated in this study. Adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} was studied in batch tests. The author of the thesis started with the simplest situation when only one metal ion was adsorbed on peat [54]. Thereafter, multimetal adsorption from spiked water solutions and spiked industrial landfill leachate solutions on different adsorbent materials was studied. One of the objectives of the investigation reported here was to select a

good adsorbent based on locally available adsorbents for the removal of metal ions in leachate from an industrial landfill. Determination of the removal efficiency of Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} by different adsorbents in batch equilibrium experiments was targeted. These toxic heavy metals can often occur in relatively high concentrations in leachate from an industrial landfill [55] as well as in leachate from municipal solid waste landfills [56]. Single- and multimetal adsorption of three metals onto the best adsorbent was investigated to obtain more knowledge on competitive adsorption in more complex systems. The role of the desorption of calcium, magnesium and 9 other metals ions was evaluated [57, 58]

1.2. Modelling of the adsorption process

In general, adsorption processes were found to proceed through varied mechanisms such as external mass transfer of solute, intraparticle diffusion and adsorption at sites. Unless extensive data are available, it is impossible to predict the rate-determining step involved in the process. However, adsorption isotherm equations, which explain the process at equilibrium conditions, provide an easier solution to this complex problem. Also, an isotherm equation does not consider the complex mechanism (external mass transfer, pore diffusion, chelation, ion exchange and chemisorption) involved in the sorption processes; engineers use the equilibrium equation with ease for the design of batch adsorption systems [59].

The relationship between the amount of a substance adsorbed per unit mass of an adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important for describing how solutes interact with the sorbent. Developing an appropriate isotherm model for adsorption is essential for the design and optimization of adsorption processes. Different isotherms can be used to describe the adsorption of metal ions onto a solid adsorbent [5, 60]. In order to describe the adsorption of metals onto peat, the Freundlich and Langmuir isotherm equations are usually used [61]. Brown, P. A. *et al.* [62] found in their review that the Langmuir isotherm generally seems to be the best choice for modelling the binding of metal ions to peat. The disadvantage of the widely used Freundlich isotherm and of many other commonly used isotherms is the application of the logarithmic function. Schulthess and Dey [63], after the investigation of different equations, stated that the use of logarithmic functions tends to very strongly reduce data variability, which can result in an apparent linearity of otherwise more complex adsorption isotherms (non-Langmuir isotherms). Additionally, the Freundlich model does not possess the correct Henry's law behaviour: at an infinitely low solute concentration the slope of the Freundlich isotherm is infinite [64].

The Langmuir model has the following form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

Where q_e represents the equilibrium solid phase concentration (mmol/g or mg/g), C_e is the concentration of metal in solution at the equilibrium (mmol/l or mg/l), q_m the maximum uptake capacity of the adsorbent (mmol/g or mg/g), and K_L is the adsorption equilibrium constant of the Langmuir isotherm (l/mmol or l/mg).

The Langmuir equation was developed for modelling the adsorption of adsorbate molecules on the energetically uniform surface. In systems as complex as peat, however, it seems unreasonable to assume that all adsorbing surface sites have the same bonding energy. If the total surface consists of two or more populations of sites with different bonding energies, the two-surface Langmuir equation as proposed by Langmuir may be used [65]:

$$q_e = \frac{q_{m_1} K_{L_1} C_e}{1 + K_{L_1} C_e} + \frac{q_{m_2} K_{L_2} C_e}{1 + K_{L_2} C_e} \tag{2}$$

Where the subscripts refer to the maximum monolayer adsorption capacity and the adsorption equilibrium constant for the two different surfaces.

For modelling the process of adsorption usually only one linear transformation is used [24, 66 – 68]. Indeed, four linear single-surface Langmuir isotherm transformations and one two-surface linear transformation could be used [69].

The Lineweaver-Burk or double reciprocal linearization:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \tag{3}$$

The Eadie-Hofstee linearization:

$$q_e = q_m - \frac{q_e}{K_L C_e} \tag{4}$$

The Scatchard linearization:

$$\frac{q_e}{C_e} = K_L q_m - K_L q_e \tag{5}$$

The Langmuir or Hanes-Woolf linearization:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (6)$$

These equations have come to be known by different names in different fields. Thus, eq (1) is called simply the binding curve in complexation studies, but is the Langmuir isotherm in sorption work and the Michaelis-Menten equation of enzyme kinetics. Equation 3 is a version of the Lineweaver-Burk display of enzyme kinetics data, the Benesi-Hildebrand plot of complexation studies and the Stern-Volmer relation of fluorescence quenching. Equation 4 is the Eadie-Hofstee plot of enzyme kinetics; with a simple rearrangement it becomes the Scatchard equation of ligand-protein binding (eq (5)). Equation 6 is the Hanes-Woolf plot of enzyme kinetics and Langmuir linearization in sorption studies. [70]. Linear regression is the most commonly used technique to estimate the sorption isotherm parameters [71]. However, previous studies have shown that the linearization of the non-linear isotherm expression produce different outcomes. The Hanes-Woolf isotherm is the most commonly used linear expression to study the relation between the concentration of solute in the liquid phase and in the solid phase at equilibrium conditions [72].

The difference between the predicted and experimental equilibrium data by different linear expressions can be due to the problems with the transformation of the non-linear to the linear expression, which will distort the experimental error as well as the normality assumptions of the least squares method. A further linear method assumes that the scatter of points around the line follows the Gaussian distribution and the error distribution is the same at every value of x. But this is rarely true or practically impossible with equilibrium isotherm models (as most of the isotherm models are non-linear) as the error distribution gets altered after transforming the data to a linear form [72, 73].

In addition, to find both single and two-surface Langmuir isotherm constants non-linear regression can be used [30, 65, 74, 75–78]. Also, it is possible to compare the data found by means of linear regressions with the data obtained using non-linear regressions. Because the Langmuir model is non-linear, fitting this model into the measured data requires a "trial and error" approach. That is, the values of the parameters are inserted into the model, the adsorbed concentrations are calculated with the model, the model-calculated values are then compared with the observed data, the model parameters are adjusted, and the process is repeated until the best agreement between the modelled and observed data is achieved [79]. Although it is commonly assumed that the linearized versions of the Langmuir model provide poorer fits and less accurate parameter estimates than the non-linear equation [59, 61, 80, 81], the most accurate Langmuir equation depends on the error structure of the data because a major assumption in regression analysis is that the variance of errors remains constant. Therefore, if a transformation improves the constancy of the error

variance, the associated linear equation will provide better fits and more accurate parameter estimates than the non-linear equation [79].

Using all possible methods described above along with the evaluation of the efficiency of different methods was one of the main tasks of this work as well as proposing a more simplified calculation by non-linear regression for constants of the two-surface Langmuir isotherm. For the modelling of adsorption and finding isotherms constants one very common reciprocal form of the Langmuir isotherm and the Freundlich isotherm were used at the beginning of the investigations [54]. Besides that, a comparison of several methods of the evaluation of data was carried out. The efficiency of the methods was evaluated by standard deviation and the coefficient of determination (R^2).

2. MATERIALS AND METHODS

2.1. Adsorbents

The adsorbents selected for the investigation of the removal of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} from the solution, and their chemical compositions are listed in Table 1.

Table 1. Composition of the filter materials used in batch tests

	Peat A	Peat B + Ash	Blue ads.	Peat A + Blue*	Red ads.	Semi-coke	Pine bark	Paper pellets
Mixture (%)	100	75/25	100	50/50	100	100	100	100
pH$_{KCl}$	5.9	7.2	2.4	na	2.1	9.5	3.4	4.5
P (mg/kg)	40	360	7 700	1740	15 000	360	380	190
N (mg/kg)	28 000	8 000	332 000	80 300	370 000	800	4 100	3 000
K (mg/kg)	30	370	1 400	320	15	8 300	1 400	200
Ca (mg/kg)	21 000	8 410	160	40	110	220 000	6 700	260
Mg (mg/kg)	2 400	980	20	5.2	19	13 000	530	430
Water content (%)	60	55	55	57	5	3	6.8	6.1
Org. matter (%)	50	39	93	72	96	14	97	86
Surface area (m^2/g)	509	290	na	na	176	124	340	311

na – not analysed

* Values are calculated from analyses of peat A and blue adsorbent

Non-dried adsorbents were used in all experiments without any pre-treatment. However, in order to make calculations for the comparisons of different materials, the water content in the materials was determined (Table 1). Since the materials chosen were intended for use in large-scale treatment plants, economy was one of the most important parameters considered when selecting the adsorbent. Natural materials (*e.g.* peat) and waste materials (carbon-containing ash, paper pellets, pine bark and semi-coke) were of special interest.

The peat materials (peat A and peat B) originated from the south of Estonia and the south of Sweden, respectively. Peat A was classified as H6–7 and Peat B as H5, according to the Von Post decomposition rating (which ranges from 1 to 10). The botanical origins of the peat samples were not determined in the study. The carbon-containing ash (ash), containing uncombusted carbon, is a waste product obtained from an incomplete combustion process associated with the pulp and paper industry in the south of Sweden. Due to its cheapness, carbon-containing ash is a good substitute for activated carbon for the removal of organic (hydrophobic) compounds. The mixture of peat and carbon-containing ash (peat B + ash) was obtained from Laqua Treatment, Sweden. Pine bark pellets (90% pine bark and 10% wood fiber) were supplied by Ecobark, Sweden. The paper pellets are used as filling in cardboard boxes used

for the transport of laboratory equipment. Semi-coke was obtained from the combustion of oil shale in thermal power plants from Northeastern Estonia.

Two white porous artificial adsorbents were obtained from Mardilaev (Tallinn, Estonia). These had been manufactured from urea-formaldehyde resin by using phosphoric acid as a catalyst. Due to other specific modifications, the adsorbents have hydrophilic (named blue) or hydrophobic (named red) surfaces. Synthetic materials such as these blue and red adsorbents, being more expensive, might be interesting materials for polishing steps.

2.2. Chemicals

Single-metal-ion stock solutions of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} were prepared by dissolving their corresponding nitrate or chloride salts, $Cu(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ and $Pb(NO_3)_2$, respectively, in deionized water. The nitrate and chloride salts were preferred for the preparation of stock solutions in order to avoid metal precipitation often associated with other anions. All salts were of analytical grade purity. The concentration of each metal ion in its stock solution was 1 g/l. These stock solutions were used for preparing multimetal ion solutions containing metals Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} in deionized water and in leachate. The leachate was brought from an industrial landfill in Sweden and information about its detailed chemical composition is presented elsewhere [55].

2.3. Experiment for measuring adsorption of metals

2.3.1. Adsorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} from multimetal solutions onto different adsorbents

Non-dried adsorbents (1 g) were placed into Erlenmeyer flasks (250 ml) and 100 ml of the multimetal solution was added to each flask. The initial concentrations of all metal ions were 5 or 100 mg/l in deionized water and about 5 mg/l in leachate solutions. The Erlenmeyer flasks were shaken on a shaking table (SV 142, Memmert WBU45) at 110 rpm for 24 hours (at 25 °C). Since the experiments were performed without buffering the pH, solutions in contact with the selected adsorbents were expected to show some pH changes. Therefore, measurements of the pH in the solutions were done before and after shaking, using a pH meter (Sentron 1001, Sentron Europe B.V., Roden, the Netherlands) with a non-glass probe. After shaking, an aliquot of 50 ml was taken from each flask and centrifuged at 2000 G for 10 min at room temperature and then filtered through a 0.45 μm polyamide 25 mm membrane filter (Himifil, Hiiumaa, Estonia). The residual concentrations of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} in the solutions were determined using a Varian Liberty II (Varian Scientific Instruments, Mulgrave, Australia) an axial inductively coupled plasma atomic emission spectrometer (ICP-AES). The precision of single measurements for

Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} using a validated method in the accredited laboratory were 4.7, 4.6, 4.6 and 6.6%, respectively.

2.3.2. Adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} from single- and multimetal solutions onto peat A

Detailed investigations of the adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} were carried out only on one adsorbent, peat A. The non-dried adsorbent (1 g) was put into Erlenmeyer flasks (250 ml) and 100 ml of multimetal or single-metal solutions were added. The water content of the peat had decreased during standing and was in this case 42% (rather than the 60% value given in Table 1). The Erlenmeyer flasks were shaken on a shaking table (SV 142, Memmert WBU45) at 110 rpm (at 25 °C). The experiments were carried out without artificially changing the pH of the solutions. The pH range during the experiments was between 5.9 and 6.7 (with an average pH value of 6.3). The rest of the experimental set up was as described above (see Chapter 2.3.1.). The influence of Cd^{2+}, Ni^{2+}, and Pb^{2+} concentrations on the adsorption to the peat from single-metal solutions was investigated using initial concentrations of 0.1, 0.2, 0.5, 1.2, 2.2 and 4.4 mmol/l of each metal ion. In our experiments multimetal solutions were prepared as follows: the solutions of one metal were prepared at concentrations of 0.1, 0.2, 0.5, 1.2, 2.2 and 4.4 mmol/l, whereas the concentrations of the other two metals were 2.2 or 4.4 mmol/l.

Different units can be used to express the concentration in adsorption studies. In a study about different adsorbents and their efficiencies in the removal of metals, the concentration was expressed using mass units (mg/l). This is especially useful when the results are intended to be compared to the limit values for pollutants in wastewater in the case of discharge to the environment. For example, governmental regulations in the Republic of Estonia enforce the following limit values for wastewater discharged to soil or water bodies: 0.2 mg/l of Cd^{2+}, 1.0 mg/l of Ni^{2+} and 0.5 mg/l of Pb^{2+}. In the second part of this thesis, molar concentrations (mmol/l) were used which are more suitable for describing multimetal and exchangeable adsorption. This approach also facilitates comparison of our results with the results of other studies, which are often given in molar concentration.

2.3.3. Adsorption of Cd^{2+} on granulated peat

Adsorption batch isotherm studies were carried out by using 12 solutions of concentrations, namely 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 mg/l. A 100 ml quantity of each solution was mixed with 1 g of granulated peat and was shaken on a shaking table (SV 142, Memmert WBU45) at 110 rpm for 4 hours. pH was not adjusted and was near 6.7. All experiments were performed at 20 °C. The number of parallel experiments in the same conditions was 8, i.e.

the data for eight identical isotherms were received. The rest of the experimental set up was as described above (see Chapter 2.3.1.).

2.3.4. Calculation and determination
of adsorption isotherm parameters

In all experiments, 1 g of a non-dried adsorbent or a mixture of adsorbents was placed in each Erlenmeyer flask. The results obtained from the experiments were then recalculated, taking into account the water content (given in Table 1) and presented on a dry-weight basis in the Results and Discussion section. In order to obtain the concentration of metal ions adsorbed onto filter materials, the following expression was used:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{7}$$

Where q_e is the mass of ions adsorbed per unit mass of a dry adsorbent (mmol/g or mg/g), C_0 is the initial metal ion concentration (mmol/l or mg/l), C_e is the metal ion concentration (mmol/l or mg/l) at equilibrium, V is the volume of the aqueous phase (l) and m is the amount (dry weight) of the adsorbent used (g).

The results from equilibrium studies on peat A were fitted into the two-parameter Langmuir equation (eq (1)).

3. RESULTS AND DISCUSSION

3.1. Modelling of the adsorption process

3.1.1. Methods for the calculation of equation constants

The adsorption of cadmium ions on granulated peat was modelled by using the Langmuir isotherms. The use of the Langmuir equation for data modelling is necessary for obtaining constants for the equation. Two methods have been used to find constants for both the single and two-surface Langmuir isotherms.

The traditional method for the calculation of the two constants (or four constants for the two-surface isotherm) uses the linear transformation of the basic Langmuir equation followed by the linear regression analysis. One of the four linearizations (eq (3) – (6)) [63, 82, 83] was used. Linearization of the Langmuir equation tends to bias the regression analysis and the subsequent estimation of the constants [63]. For instance, several authors have noted that having q_e or C_e appear on both axes tends to decrease data variability [63, 84]. To find constants for the two-surface Langmuir equation, the transformed linear isotherm was resolved into two slopes [85]. The constants were usually calculated from graphics prepared by plotting q_e / C_e versus q_e (Fiq.1) by using auxiliary equations [60, 86 – 88]
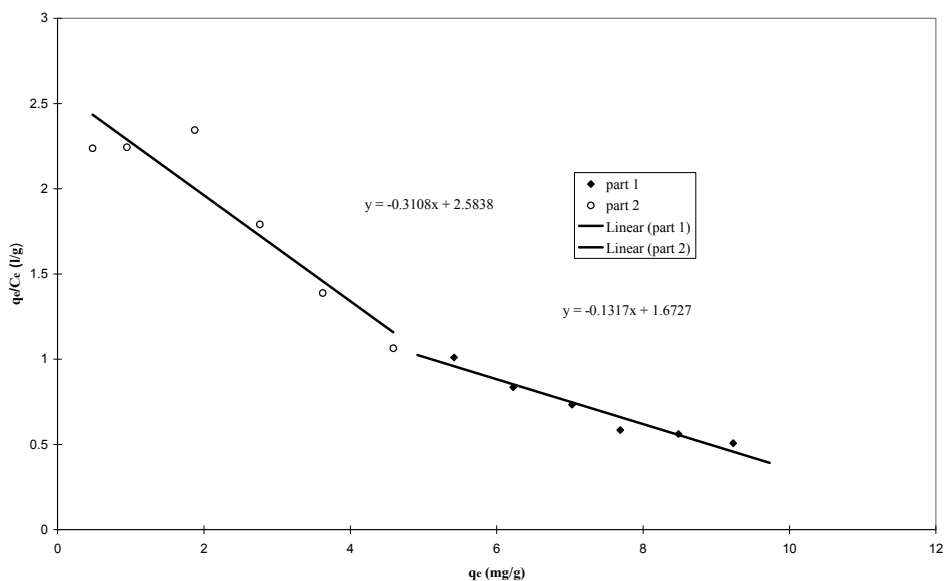

Fig. 1. Scatchard plot resolved into two straight lines as proposed by Sposito

Rather than calculate the constants from the linear portions of the curve, several authors have calculated them directly from equations (1) or (2) by using non-

linear regression [61, 63, 68, 69]. The computer programmes like STATISTICA [30], SYSTAT [77], MINTEQA2 [78] have been used by some authors to perform non-linear regression calculations.

3.1.2. Comparison of methods

The number of parallel experiments made in the same conditions was 8, namely data for eight identical isotherms were received. Samples were taken at 12 different concentrations.

   Several methods of the evaluation of data were compared. The efficiency of the methods was evaluated by standard deviation. The following equation [89] shows the difference between the estimated curve and the experimental data:

$$ s = \sqrt{\frac{\sum\limits_{i=1}^{n} (q_{ei} - q_{ei}^{1})^2}{n-1}} \tag{8} $$

Where q_{ei} is the amount of the metal adsorbed corresponding to the equilibrium concentrations of adsorbate C_{ei}

s –   standard deviation

q_{ei}^{1} – amount of the metal adsorbed, calculated with the Langmuir isotherm equation

n –   number of data points; $n = 12$

Results are shown in Table 2:

Table 2. Comparison of different methods for the calculation of the Langmuir isotherm constants.

Linear regressions	Plot axes	q_m (mg/g)	K_L (l/mg)	Correl. coef. R^2	s
Lineweaver-Burk	$1/q_e$ vs $1/C_e$	10.88	0.22	0.9971	0.39
Eadie-Hofstee	q_e vs q_e/C_e	10.04	0.25	0.9328	0.43
Scatchard	q_e/C_e vs q_e	10.41	0.23	0.9328	0.38
Langmuir	C_e/q_e vs C_e	11.17	0.20	0.9838	0.33
Nonlinear regression	q_e vs C_e	11.68	0.17	–	0.28

The Lineweaver-Burk linearization (Fig. 2) seems to fit the data best when the correlation coefficients of regression (R^2 = 0.9971) are compared. This assumption is wrong because a high R^2 value for a particular model does not necessarily mean that this model is the best [90]. For example, Viraraghavan

and Rao [23] received **negative** maximal adsorption values by using the same linearization, the linearization coefficients for negative q_m values they received were up to 0.938. Comparison of standard deviations demonstrates that the Lineweaver-Burk, Eadie-Hofstee and Scatchard linearizations do not fit the data so well (s = 0.38 – 0.43). It has been found by several authors that the double Lineweaver-Burk plot is generally considered to be less desirable for the modelling of adsorption data than the Scatchhard plot (Fig. 1) because even a small error in the low aqueous concentration range can significantly affect the entire regression analysis [79, 83, 91]. Unfortunately, in the case of the Eadie-Hofstee and Scatchard linearization, x and y data are not independent and the correlation between x and y is underestimated, i.e. the equation may provide a poor fit to the data that do confirm the Langmuir model [81]. Better results among linearizations were found with the Langmuir linearization (s = 0.33), but the results obtained by using the non-linear regression were still the best (s = 0.28). Several authors [59, 72, 73, 79] have supported this conclusion.

Fig. 2. Lineweaver-Burk linearization of the Langmuir isotherm
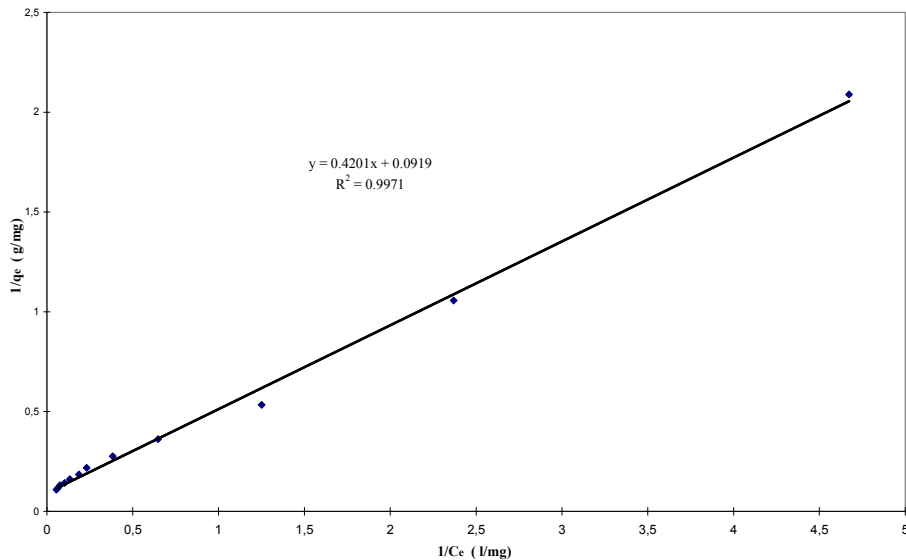
The constants of the two-surface Langmuir isotherm were calculated by using the system of equations created by the author of the thesis and its detailed description is presented elsewhere [92]. Alternatively, the Langmuir two-surface equation was solved by plotting q_e / C_e versus q_e (Fig. 1) as proposed by Sposito [60, 86]. The results are shown in Table 3:

Table 3. Comparison of two methods for the calculation of the two-surface Langmuir isotherm constants

Method	q_{m1}(mg/g)	q_{m2} (mg/g)	K_{L1}(l/mg)	K_{L2} (l/mg)	s
New method created by authors	2.71	9.66	0.48	0.11	0.17
Method proposed by Sposito	8.31	12.87	0.31	0.13	0.24

A new method described above fits the data better than the method used by Sposito [60] with the standard deviations being 0.17 and 0.24, respectively. In Sposito's method linearization was an additional source for mistakes [63]. Furthermore, it is not always clear which points belong to the first part of the divided isotherm and which to the second part of it (Fig. 1).

The results of both calculations given above were compared to the standard deviation obtained according to the Langmuir one-surface isotherm (s = 0.28) and it appeared that the data fit better the two-surface Langmuir equation than the one-surface Langmuir equation. Several studies have confirmed an excellent fit of the two-surface Langmuir model for the adsorption data of cadmium and other heavy metals [75, 76, 88, 93].

3.2. Selection of the adsorbent

Nine different adsorbents were used for the investigations. The cadmium adsorption on granulated peat was investigated separately.

3.2.1. Adsorption studies for a selection of filter materials intended for metal removal

3.2.1.1. Adsorption capacity

Results of multimetal adsorption from spiked water solutions (with initial concentrations of each metal of about 5 or 100 mg/l) and spiked leachate solutions (with initial concentrations of each metal of about 5 mg/l) on different adsorbent materials are presented in Fig. 3.
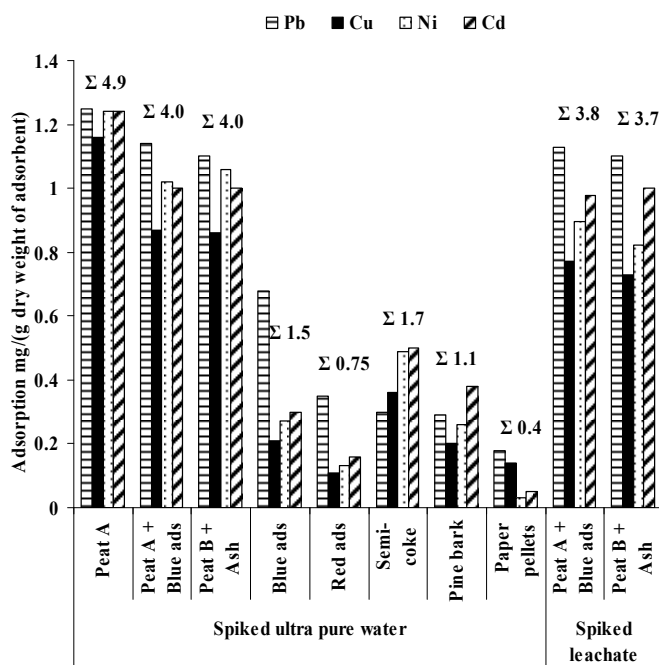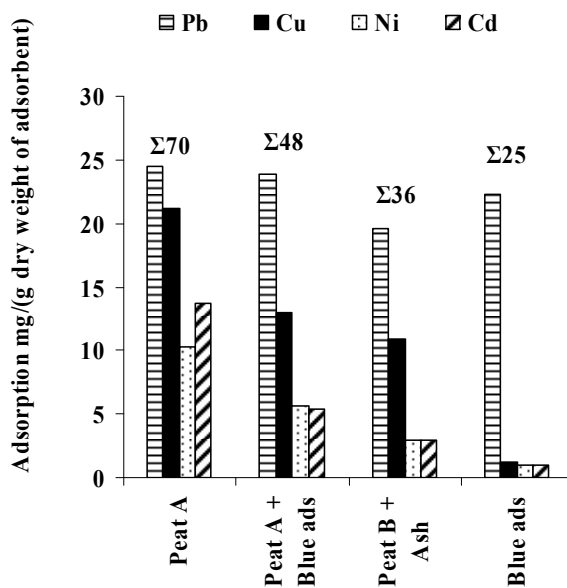
Fig. 3. Adsorption of metals (Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+}) on different adsorbents (mg/g) from multimetal water and leachate solutions with initial concentrations of each metal of about 5 mg/l (a) and from a multimetal water solution with initial concentrations of each metal of about 100 mg/l (b)

The results in Fig. 3a show that with an initial concentration of metal ions of about 5 mg/l, peat A along with the mixtures of peat A + blue adsorbent and peat B + ash, have a significantly higher total adsorption capacity for the four metals considered than the other materials investigated. Materials such as paper pellets, semi-coke, pine bark, blue and red adsorbents have a significantly lower amount of ions adsorbed per mass of adsorbent (mg/g). The highest adsorption of metal ions was displayed by peat A. The amount of the different metals adsorbed by mixtures of peat A + blue adsorbent and peat B + ash were the same. However, for adsorbents in which two materials were mixed, peat is most probably the main component adsorbing metal ions. The amount of Cd^{2+} adsorbed by granulated peat from a single-metal solution was low, only 0.48 mg/g.

The adsorption capacities of four adsorbent materials were also investigated for solutions characterized by initial concentrations of about 100 mg/l for each metal. The results (Fig. 3b) show that when the initial concentrations of metals in the solution increased 20 times, there was an increase in the amount of metal ions removed by the fixed amount of an adsorbent (mg/g). An increase in metal uptake with an increase in metal concentration is a common phenomenon observed with a variety of adsorbents [44]. The removal of Pb^{2+} (mg/g) from multimetal solutions was significantly higher than the removal of the other metals. Although the amount of adsorbed metal ions increased, this increase in the adsorption of metals on the adsorbent materials tested was far from what was expected (i.e. approximately a factor of 20), except for lead ions. For instance, the adsorption of Cu^{2+} on the mixture of peat B + ash (mg/g) increased 13 times instead of 20 times. Obviously, the capacity of the adsorbents had been exceeded and lead was probably adsorbed preferentially at the available sites. The amount of Cd^{2+} and Ni^{2+} adsorbed per gram of a dry adsorbent was significantly lower than that for Pb^{2+} and Cu^{2+}. The amount of Cd^{2+} adsorbed by granulated peat from a single-metal solution was 8.5 mg/g.

Since the goal from a long-term perspective was to use the adsorbents in filters for leachate treatment, experiments were also performed using leachate. Fig. 3a gives the of results using leachate spiked with metal ions to obtain concentrations of about 5 mg/l. Because the concentrations in landfill leachate of the considered metals usually remain below 1 mg/l and very seldom exceed about 5 mg/l, the initial metal ion concentrations of 100 mg/l in leachate solution were not studied further.

The results obtained with spiked water and spiked leachate (Fig. 3a) show that the removal efficiency might be somewhat lower in leachate water for two of the metals, namely Cu^{2+} and Ni^{2+}. This is not unexpected since leachate is known to contain a number of other ions which might compete with the ions considered in this experiment [24]. Additionally, another probable reason might also be that the leachate contained relatively high concentrations of chloride ions (410 mg/l) and ammonium-nitrogen (90 mg/l). The heavy metal ions under consideration are known to form stable complexes with both these types of ligand. Consideration of the pH of the solution is an important factor since an

increase in pH leads to a decrease in the ammonia concentration, (at the expense of the ammonium ion adsorbed) [90, 94, 95]. On the other hand, the adsorption of ammonium ions increases the number of occupied adsorption sites and thus decreases adsorption of all metal ions. Values of the pH in solutions before and after shaking with adsorbents were different in spiked water and a spiked leachate solution (Fig. 4), which circumstance might have affected the amount of the metal adsorbed.
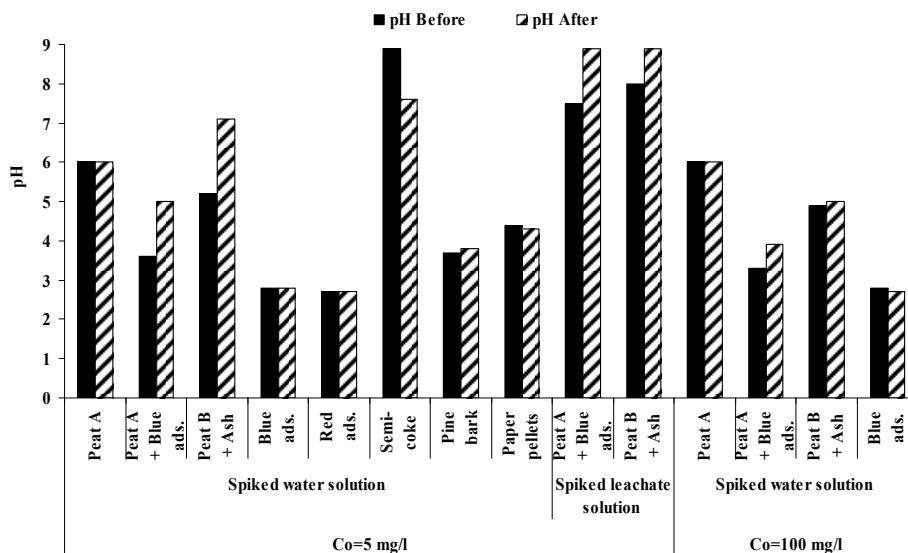
Fig. 4. Changes in pH during the experiments. Values of the pH of spiked water solution with initial concentration (C_0) of about 5 and 100 mg/l before adding adsorbents were 5.2 and 5.0, respectively. The pH of the raw leachate was 8.0.

3.2.1.2. Percentage removal

The percentage reductions of the investigated metal ions in spiked water solutions and in spiked leachate by the two main adsorbents of interest are given in Table 4. The results show that a high percentage removal of metal ions (> 90%) was achieved when the initial concentrations of metal ions in spiked water were about 5 mg/l, and the percentage removal was still above 75% for the spiked leachate solution. When the metal ion concentration was higher, *e.g.*, about 100 mg/l, the adsorption capacity was exceeded, as discussed previously, and the reduction of metal ion concentration was less effective, except for lead ions.

Table 4. Reduction (%) of metal ions from spiked multimetal water and leachate solutions at the initial concentration of each metal of about 5 or 100 mg/l.

	Spiked water solution				Spiked leachate solution	
	5 mg/l of each metal		100 mg/l of each metal		5 mg/l of each metal	
	Peat A + Blue	Peat B + Ash	Peat A + Blue	Peat B + Ash	Peat A + Blue	Peat B + Ash
Pb^{2+}	99.0	99.6	99.0	84.8	97.7	99.8
Cu^{2+}	95.9	99.5	69.9	61.1	85.2	84.9
Ni^{2+}	89.6	96.4	24.6	13.6	78.3	75.1
Cd^{2+}	93.0	98.0	21.9	12.4	91.3	97.6

The percentage removal of Cd^{2+} in a single-metal solution by granulated peat was 95.7 % when the initial concentration of cadmium ions was about 5 mg/l and 84.9 % and when the initial concentration of cadmium ions was about 100 mg/l.

3.2.2. Selection of filter materials

The results showed that the adsorption capacity of metals was higher for peat A, and for a mixture of peat A and blue adsorbent and for a mixture of peat B and ash than for the other adsorbents studied. Due to economic considerations, a filter-bed-based landfill leachate treatment system is preferably filled with a low-cost adsorbent, which requires little processing and is abundant in nature, or is an abundant by-product or waste material from industry [18]. Blue adsorbent does not fulfil these requirements. However, due to a high adsorption capacity, a mixture of peat A+ blue adsorbent is recommended for utilization in the polishing step of a landfill leachate treatment system. Moreover, peat A and peat B + ash are locally available in large amounts for use in a filter-bed for the treatment of landfill leachate in Estonia and in Sweden, respectively. The results obtained have thus shown that peat generally seems to be the best adsorbent for metal ions, and further studies of peat as an adsorbent are presented herein.

3.3. Adsorption of Cd^{2+}, Pb^{2+}, and Ni^{2+} from single-metal solutions onto peat A

To investigate the adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} from single-metal solutions, six different initial adsorbate concentrations (between 0.1 and 4.4 mmol/l) were investigated. The adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} on peat was modelled by using the Langmuir isotherms. The constants, calculated directly from the Langmuir equation by using the non-linear regression, are shown in Table 5.

Table 5. Langmuir equation constants

Metal ion	Langmuir constants	
	q_m (mmol/g)	K_L (l/mmol)
Pb^{2+}	0.571	31
Cd^{2+}	0.374	4.4
Ni^{2+}	0.359	2.8

The value of Langmuir constants q_m, indicating the maximum adsorption capacity, were found to decrease in the order $Pb^{2+} > Cd^{2+} \geq Ni^{2+}$. Generally, the maximum adsorption capacities of Cd^{2+}, Pb^{2+}, and Ni^{2+} for different lignin-based and peat adsorbents were, with slight variations, found to follow the same order [29, 42, 96, 97]. This order can be explained by the differences in ionic radii (r_i) of metals. For instance, Pb^{2+} has the biggest ionic radius (0,0120 nM), followed by those of Cd^{2+} (0.0097 nM) and Ni^{2+} (0.0069 nM) [37]. For the larger unhydrated ions, since the charge is more dispersed, hydration water is held less strongly [98]. The bigger the ionic radius, the stronger the adsorption of the ion since the hydration capacity of that ion is smaller, resulting in weaker binding of the ion and the water phase. The decrease in the adsorption of metals obtained in this study, is also consistent with the ionic radii of hydrated ions (r_h): Pb^{2+} (0.274 nM), Cd^{2+} (0.228 nM) and Ni^{2+} (0.206 nM) or with the inverse of the hydrated radii (r_h) multiplied by the number of waters of hydration [49].

The effect of the initial concentrations of Cd^{2+}, Pb^{2+}, and Ni^{2+} in solutions on their adsorption on peat A was studied and the results are presented in Table 6.

Table 6. Reduction (%) of metal ions (Cd^{2+}, Ni^{2+}, and Pb^{2+}) by peat A from single-metal solutions at different initial concentrations (C_0) of each metal

	C_0 (mmol/l)					
	0.1	0.2	0.5	1.2	2.2	4.4
Pb^{2+}	97.5	98.1	98.5	98.8	97.5	73.3
Cd^{2+}	95.1	93.6	91	83	68.3	45.7
Ni^{2+}	88.3	88.9	84.9	75.6	62.2	42.8

The results in Table 6 show that the percentage of metal ions removed by peat A decreases with an increasing initial concentration. Peat A is able to remove almost all metal ions at the lowest metal ion concentration. The number of binding sites on the peat, in this case, is obviously sufficient. The percentage adsorption of Pb^{2+} (between 73.3 and 98.8%) was always the highest at all

concentrations studied compared to the other metal ions. The percentage adsorption of the metal ions decreased noticeably for Ni^{2+} and Cd^{2+} (down to 42.8% and 45.7%, respectively) when increasing the initial concentrations of the metals in solutions to 4.4 mmol/l.

3.4. Adsorption of Cd^{2+}, Pb^{2+}, and Ni^{2+} from multimetal solutions onto peat A

The presence of a single-metal ion in natural water or wastewater is a rare situation. In the case of multimetal adsorption, one should take into consideration the effects of other metals on the adsorption of a given metal. At lower initial concentrations, there is literally no influence of metals on each other, but at increasing initial concentrations the level of saturation for adsorption centres seems to be reached and the influence of the presence of other metals becomes substantial. When metals compete for the same adsorption sites of an adsorbent, metals with a greater affinity (strongly adsorbed species) can displace others with a lower affinity (weakly adsorbed species). The adsorption affinities are tentatively correlated to their properties such as the ionic radius, the hydrated radius etc. [1] (see also Chapter 3.3.).

In multimetal experiments, the initial concentration of one metal in the solution was changed from 0.1 to 4.4 mmol/l, whereas the concentration of the other two metals was held constant at 2.2 or 4.4 mmol/l. The results obtained from the experiments are given in Table 7. The results show that an increase in the initial concentration of one metal ion decreases the percentage adsorption (q_e%) of all other metal ions. For example, increasing the initial concentration of lead ions by 45 times while holding the initial concentrations of Ni^{2+} and Cd^{2+} constant, decreases the q_e% for Pb^{2+} from 97 % to 64 %, for Ni^{2+} from 29 % to 9% and for Cd^{2+} from 35 % to 5% (Table 7, third column from the right). Co-adsorption induces a decrease in the concentration of a metal in solution at equilibrium (q_e) for each metal ion, but the extent of the decrease depends on other metal ions present in the solution. Qin, F. *et al*., Liu, Z-R. *et al*., Gupta, B.S. *et al*., McKay, G. and Porter, J.F., Balasubramanian, R. *et al*., Ho, Y.S. and McKay, G. have reported similar results using peat as an adsorbent [1, 3, 8, 25, 26, 53].

Increasing the initial concentrations of metals in the solution increases the number of occupied adsorption sites and thus decreases the adsorption of all metal ions in the solutions onto peat. Among the selected metals, the hydrated radius of Pb^{2+} (0.274 nM) was the greatest, and therefore Pb ions have more accessibility to the surface and pores than the other two cations which leads to a higher adsorption of lead. Cd (0.228 nM) and Ni (0.206 nM) ions with lower hydrated radii compete equally, though less favourably, for adsorption sites. The order of adsorption is thus the same in the case of competitive multimetal adsorption as it is for single-metal adsorption: $Pb^{2+} > Cd^{2+} \geq Ni^{2+}$. The same

order of adsorption was also reported by Qi, B.C. and Aldrich, C. [42] in the case of multimetal adsorption on tobacco dust.

The conclusions introduced in the previous paragraph can also be confirmed by looking at the two quantitative parameters, which characterize multimetal adsorption. These parameters are the relative metal adsorption R_i and the relative coverage θ_i, which were calculated according to the following equations:

$$R_i = \frac{\text{metal } i \text{ adsorption capacity with the coexistence of metals } j \text{ and } k}{\text{metal } i \text{ adsorption capacity in the absence of metals } j \text{ and } k} \times 100\% \qquad (9)$$

$$\theta_i = \frac{\text{moles of metal i adsorbed}}{\text{Sum of moles of all three metals adsorbed}} \times 100\% \qquad (10)$$

According to Fowle, D.A. and Fein, J.B. [99], the interactions between different metals in a solution can be characterized as follows:
(i)   The effect of a mixture is greater than that of each of the individual effects of the constituents in the mixture (synergism, $R_i \% > 100$);
(ii) The effect of a mixture is less than of each of the individual effects of the constituents in the mixture (antagonism, $R_i \% < 100$);
(iii) The effect of a mixture is equal to that of each of the individual effects of the constituents in the mixture (non-interaction, $R_i \% = 100$).

R_{Ni} ranged from 22% to 72% for all the concentrations investigated (see Table 7), and the total interactive effects of Cd^{2+} and Pb^{2+} on the adsorption of Ni^{2+} by peat were antagonistic. R_{Cd} ranged from 11% to 75% for all the concentrations investigated. Therefore, addition of other metals decreased the adsorption of cadmium ions onto peat and the general effect was antagonistic as well. Addition of Cd^{2+} and Ni^{2+} to the lead solution gave R_{Pb} values ranging from 87 to 103%. The addition of other metals increased the adsorption of Pb^{2+} and a synergistic effect was observed (R_{Pb} value 103%) at the initial Pb^{2+} concentration of 0.096 mmol/l. With an increasing initial concentration of Pb^{2+}, the general effect on Pb ions decreases until it becomes nonexistent at an initial Pb^{2+} concentration of 0.198 mmol/l, and at even higher concentrations there was an antagonistic effect. When all the metals were in the solution at maximum concentrations, R_{Pb} was 87%. Qi, B.C. and Aldrich, C. [42] reported only an antagonistic behaviour of Cd^{2+}, Pb^{2+}, and Ni^{2+} in the case of multimetal adsorption on tobacco dust.

Table 7. Adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} by peat A from multimetal solutions when the initial concentration of one metal in the solutions was increased in stages from 0.1 to 4.4 mmol/l and the initial concentrations of the other two metals were held constant at 2.2 (Pb) or 4.4 mmol/l (Ni, Cd)

Metal	C_0 (mmol/l)	C_e (mmol/l)	q_e (mmol/g)	$q_e\%$ (%)	θ_i	R_i (%)
Cd^{2+}	**0.101**	0.078	0.004	23	1	25
Ni^{2+}	4.419	3.525	0.154	20	31	48
Pb^{2+}	2.175	0.189	0.341	91	68	94
Cd^{2+}	**0.202**	0.158	0.008	22	2	24
Ni^{2+}	4.445	3.573	0.15	20	30	47
Pb^{2+}	2.192	0.203	0.342	91	68	94
Cd^{2+}	**0.507**	0.389	0.02	23	4	25
Ni^{2+}	4.47	3.53	0.161	21	31	50
Pb^{2+}	2.193	0.205	0.341	91	65	94
Cd^{2+}	**1.199**	0.976	0.038	19	8	22
Ni^{2+}	4.44	3.683	0.13	17	26	40
Pb^{2+}	2.174	0.227	0.335	90	67	92
Cd^{2+}	**2.242**	1.856	0.066	17	13	25
Ni^{2+}	4.527	3.799	0.125	16	24	39
Pb^{2+}	2.21	0.258	0.335	88	64	43
Cd^{2+}	**4.554**	3.826	0.125	16	22	35
Ni^{2+}	4.601	3.906	0.119	15	21	37
Pb^{2+}	2.258	0.328	0.332	85	58	92

Metal	C_0 (mmol/l)	C_e (mmol/l)	q_e (mmol/g)	$q_e\%$ (%)	θ_i	R_i (%)
Ni^{2+}	**0.092**	0.057	0.006	39	1	39
Cd^{2+}	4.338	3.432	0.156	21	32	44
Pb^{2+}	2.149	0.231	0.33	89	67	91
Ni^{2+}	**0.199**	0.126	0.012	36	3	40
Cd^{2+}	4.435	3.606	0.142	19	29	40
Pb^{2+}	2.191	0.243	0.335	89	68	92
Ni^{2+}	**0.492**	0.358	0.023	27	5	31
Cd^{2+}	4.365	3.558	0.139	18	28	39
Pb^{2+}	2.158	0.238	0.33	89	67	91
Ni^{2+}	**1.225**	0.972	0.043	21	9	27
Cd^{2+}	4.467	3.701	0.132	17	26	37
Pb^{2+}	2.165	0.259	0.328	88	65	90
Ni^{2+}	**2.219**	1.837	0.066	17	13	27
Cd^{2+}	4.441	3.71	0.126	16	25	35
Pb^{2+}	2.143	0.279	0.32	87	63	88
Ni^{2+}	**4.601**	3.906	0.119	15	21	37
Cd^{2+}	4.554	3.826	0.125	16	22	35
Pb^{2+}	2.258	0.328	0.332	85	58	92

Metal	C_0 (mmol/l)	C_e (mmol/l)	q_e (mmol/g)	$q_e\%$ (%)	θ_i	R_i (%)
Pb^{2+}	**0.096**	0.002	0.016	97	3	103
Cd^{2+}	4.462	2.915	0.266	35	52	75
Ni^{2+}	4.569	3.228	0.23	29	45	72
Pb^{2+}	**0.198**	0.006	0.033	97	7	100
Cd^{2+}	4.523	3.144	0.237	30	49	67
Ni^{2+}	4.636	3.404	0.212	27	44	66
Pb^{2+}	**0.484**	0.019	0.08	96	17	95
Cd^{2+}	4.467	3.232	0.212	28	44	60
Ni^{2+}	4.539	3.455	0.186	24	39	58
Pb^{2+}	**1.169**	0.085	0.186	93	38	95
Cd^{2+}	4.379	3.49	0.153	20	31	43
Ni^{2+}	4.505	3.616	0.153	20	31	47
Pb^{2+}	**2.258**	0.328	0.332	85	58	92
Cd^{2+}	4.554	3.826	0.125	16	22	35
Ni^{2+}	4.601	3.906	0.119	15	21	37
Pb^{2+}	**4.395**	1.604	0.48	64	81	87
Cd^{2+}	4.398	4.163	0.04	5	7	11
Ni^{2+}	4.546	4.14	0.07	9	12	22

C_0, initial concentration of metals in solution; C_e, concentration of metal ions in solution at equilibrium; q_e, amount of ions adsorbed per unit mass of dry adsorbent; $q_e\%$, percentage adsorption of metal; R_i, relative metal adsorption and θ_i, relative coverage

Selective adsorption in the ternary system was also evaluated in terms of relative coverage θ_i of each metal as demonstrated in Table 7. At the constant initial concentration of Ni^{2+} and Cd^{2+}, the relative coverage of Pb^{2+}, θ_{Pb}, increased with an increasing initial lead ion concentration (from 3% to 81%, see Table 7). A similar adsorption pattern was also observed for the simultaneous adsorption of Ni^{2+} and Cd^{2+}. An increase in the initial concentration of lead ions at constant Ni^{2+} and Cd^{2+} initial concentrations decreased θ_{Ni} from 45% to 12% and θ_{Cd} from 52% to 7%, or approximately 3.8 times for Ni^{2+} and 7.4 times for Cd^{2+}. Increasing of the initial concentration of the cadmium ion at constant Ni^{2+} and Pb^{2+} initial concentrations decreased the value of relative coverage θ_{Ni} from 31% to 21% and θ_{Pb} from 68% to 58% (see Table 7), or approximately 1.5 times for Ni^{2+} and 1.2 times for Pb^{2+}. For increasing initial concentrations of nickel, the relative coverages were very similar. An increase in the initial concentration of the nickel ion at constant Cd^{2+} and Pb^{2+} initial concentrations decreased the value of θ_{Cd} from 32% to 22% and θ_{Pb} from 67% to 58% – approximately 1.5 times for Cd^{2+} and 1.2 times for Pb^{2+}. Such a change of relative coverage for different metal ions means that, with an increase in concentration, competition for the binding sites increased. An increase in the initial concentration of one metal ion in the solution decreases the amount of other metal ions adsorbed from the solution onto peat A. This is most probably due to an increase in the number of occupied adsorption sites and an increased competition for free adsorption sites. The driving force for the adsorption of Pb ions on peat A exceeds those for the adsorption of Cd and Ni ions onto peat. Adsorption of Cd and Ni ions are characterized by a substantially equal driving force. According to the characteristics R_i and θ_i, the order of the driving force of adsorption onto peat was the same as in the case of single-metal adsorption: $Pb^{2+} > Cd^{2+} \geq Ni^{2+}$.

3.5. Exchangeable ions from peat A

Using the possibilities given by the ICP-AES method, the most important metal ions and a phosphate anion desorbed from peat were determined in addition to the three metals ions investigated. The concentration of desorbed Al^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} and a phosphate anion was less than 0.1 µmol/g. Also, the desorption of Ba^{2+} (0.3 µmol/g), K^+ (1 µmol/g), Na^+ (3 µmol/l), and Zn^{2+} (0.5 µmol/l) was low. Increasing of the concentration by adding Cd^{2+}, Ni^{2+}, and Pb^{2+}, increased the concentrations of Ba^{2+}, K^+, and Na^+ in the solution at the equilibrium state only 2 times (10 times for Zn^{2+}).

The peat used for the investigations (see Table 1) contained mostly calcium, magnesium and iron, the desorption of iron was poor (0.09 µmol/g) and it did not increase even after adding the three investigated metals ions to the solution. For peat A, Ca^{2+} and Mg^{2+} were the most exchangeable ions. Balasubramanian, R. *et al*., Chen, X-H. *et al*. [22, 26] observed that there was more Ca^{2+} released

than other cations, which is consistent with the fact that Ca is the major cation present in peat. The blank test showed that 0.07 mmol/g of Ca and Mg ions were desorbed from the peat to deionized water. The concentrations of the desorbed Ca and Mg ions after shaking the peat with multimetal solutions (4.4 mmol/g each metal ions) were 0.559 and 0.033 mmol/g, respectively. The concentrations of the trapped Cd, Ni, and Pb ions were 0.040, 0.070 and 0.480 mmol/g, respectively. Thus, the total concentration of the desorbed Ca and Mg ions were 0.592 mmol/g and the total concentration of the adsorbed Cd, Ni, and Pb ions were 0.590 mmol/g. This indicates that Ca^{2+} and Mg^{2+} were substituted by Cd^{2+}, Ni^{2+}, and Pb^{2+} relatively equally. Balasubramanian, R. *et al.* [26] noted that for the exchangeable adsorption phenomenon, the relative quantities of the heavy metal ions taken up by the adsorbent and the alkaline-earth metals released into the aqueous solution should be approximately equal. This strongly suggests that for peat A exchangeable adsorption is one of the most important processes taking place. Similar results for peat have also been reported by other researchers [3, 62, 100, 95]. Zhipei, Z. *et al.* [101] studied 12 types of peat and found a strong correlation between the exchangeable Ca and Mg ions on the peats and their adsorption capacity for Cd^{2+}, Ni^{2+}, and Pb^{2+}. Wolf, A. *et al.* [100] studied the selective uptake of heavy metal ions over the pH range 4–5 and found that Ca^{2+} considerably influenced the adsorption of heavy metal ions by peat. An increasing ratio of Ca^{+}/H^{+} in peat enhances the sorption of heavy metal ions and an increasing Ca^{2+} concentration in the solution will reduce their adsorption. According to Wolf, A. *et al.* [100], for Ca^{2+} concentrations above about 0.01 N, the order of selectivity in peat was $Cu^{2+} > Pb^{2+} > Zn^{2+}$ and Cd^{2+}, whereas in the absence of Ca^{2+}, the order of selectivity was $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$.

4. APPLICATIONS AND FUTURE DIRECTIONS

The results of this study were planned to be applied in two ways. First, for developing the purification system for leachate water, which aim was achieved completely. Second, for the investigations of deposition and adsorption/ desorption onto peat and forest soils of Northeastern Estonia rich in humic substances. This aim was achieved partially, as concentrations of metals in the bog water are extremely low. During the investigations we were lacking the equipment for a statistically reliable detection of these concentrations. As ICP-MS nowadays is a very fast-developing technique, the corresponding equipment is in production already and the author has ordered it already.

4.1. Treatment of industrial landfill leachate

The objective of the current investigation was to select a good adsorbent based on locally available adsorbents for the removal of metal ions in leachate from an industrial landfill. Equilibrium batch adsorption studies were carried out by exposing different adsorbents to solutions of copper, cadmium, nickel and lead. The same experiments were also performed using leachate. Nine adsorbents were used for the experiments. One promising adsorbent (peat A) was selected for further investigations of equilibrium times and adsorption behaviour. Single- and multimetal adsorption of three different metals onto the selected adsorbent was studied as well [57, 58].

Laboratory results constitute the basis for pilot-plant experiments at a landfill site. The design of a natural leachate treatment system for a specific landfill site is a complex matter, thus knowledge obtained merely from laboratory studies, which were often carried out far away from the actual landfill site, is insufficient. A long-term on-site pilot-plant was accordingly set up to obtain more site-specific knowledge before a full-scale biofilter-based treatment plant was constructed. Such a study was important to confirm that under specific site conditions, an efficient treatment could be achieved by the proposed filter-bed system [102].

As the last step a full scale on-site treatment plant was launched to treat leachate from an industrial mono-landfill containing shredder residue of dismantled end-of-life vehicles and white goods. The treatment plant consists of a 500 m^3 equalisation pond and a vertical-flow biofilter system filled with a mixture of peat and carbon-containing ash. The biofilter system was constructed at the end of 2002 by Laqua Treatment AB (Sweden). The performance of a full-scale treatment plant was evaluated over a long period from several points of view. [56, 103, 104] The pilot-plant experiments and evaluation of the full-scale treatment plant were carried out by Pille Kängsepp and her co-authors [105].

4.2. Investigations of deposition of metals at bog massifs, peat production fields and humic-substance-rich forest soils of North-East Estonia.

The main research was carried out in the North-East of Estonia. Most of the territory is covered by forests and peatlands, rural settlement is sparse (2–10 persons per km^2). The northern part is heavily industrialised. Open-pit mines and peat fields cover large territories [106]. *Kukersite* oil shale is mined (25–65% of organic matter, energetic value 11–15 MJ/kg). Oil shale is used as fuel for energetics (the Estonian and Baltic thermal power plants and a few smaller ones) and raw material for chemical industry (benzoic acid, nitric fertilizers and shale oil are produced). The mineral part of oil shale is rich in chemical components, with carbonates and silicates of calcium, magnesium and other metals dominating. A number of trace metals (Pb, Cd, Zr, Zn, Cu, Ni, Sr, Th) occur in significant concentrations [107]. Oil-shale ash is used as a component for cement, produced in Kunda. The background site used for comparative measurements was located in the Alam-Pedja nature reserve, about 100 km SW from the main site.

Strong alkaline pollution near two oil-shale-fired power plants (the Baltic and the Estonian PP) and Kunda cement industry (the Kunda Nordic Cement) was observed. Loads of calcium, magnesium, sulphate and various trace metals, exceeding the background values more than one decimal order, were pointed out. Alkaline precipitation, caused by oil-shale fly ash and cement dust containing 30 and 42% of CaO respectively [107, 108] and by other alkaline oxides and various trace metals has seriously damaged the forest and bog ecosystems in Northeastern Estonia. Deposition fluxes of 27 chemical species were used for the factor, cluster and correlation analyses.

4.2.1. Factor analysis and source-receptor relations

Statistical methods were used to estimate which part of the pollution originates from the known regional sources and distinguish the groups of chemical species that are related with different technological processes or different transport mechanisms.

The principal component method of factor analysis (PCA) [109] was used to obtain a synopsis of the data and identify the sources. 55 samples and 27 chemical components for the hierarchical cluster analysis in the Eulerian space of variables [110] were used to classify the chemical species.

The first four resulting factors explained 95,1% of the total variance. Factor 1 explained 74,6 of the total variance. Considering the plot of factor scores of factor 1 and factor 2 (10.5%), factor 1 is related mainly with four different layers of the sample taken from the immediate neighbourhood of the Kunda Nordic Cement Plant and thus have very high loads of calcium. The other

samples are distinguished mainly by means of factor 2. A clear tendency of the total pollution level increase with factor 2 score has been established.

Factor 1 is highly correlated with Mg, Ca and several trace metals like Ni, Cu etc. that are emitted in large amounts in the contents of cement dust. Factor 2 has high correlations with sulphate, chloride and some such metals as Cu, Pb, Cd etc., occurring in considerable concentrations in oil-shale fly ash. A number of metals have considerable correlations with both factors 1 and 2 (the mineral compositions of cement dust and fly ash are quite similar because oil-shale ash is used as a component of cement).

Factor 3 (5.9% of variance, correlated with Zn, Cd, Pb, Cu and some other metals) represents components that have significant sources besides power plants and cement industry (traffic, far transport). Factor 4 is almost uniquely determined by nitrate, which may originate from different sources (far transport, traffic, domestic heating), because the emission level from point sources is relatively low.

4.2.2. Cluster and correlation analysis

The cluster dendrogram of components shows 3 main groups that may be interpreted as (1) macro-components and some related micro-components of oil shale mineral part (Ca, Mg, Fe, U, Ni, Sr), (2) reaction products of gaseous components (sulphate, chloride) with some metals (Pb, Cd, As), and (3) micro-components of oil-shale mineral part (Ce, Nd, Y, Zr, Cu etc.). Zn exists separately from groups, nitrate has a weak connection with group (3). Groups can be formed due to different behaviour of fly ash fractions that could be more easily transported by air masses. Ca and, probably, some other macro-components have a larger share in the coarse fraction of fly ash and especially in cement dust.

A greater majority of correlation coefficients between 27 components were positive and statistically significant at the confidence level of 95%. A large group of species (Ca, Mg, Sr, Mn, Ni, Co, U, Ba, Fe) have correlations exceeding 0.9 with each other. Cu, Zr and Zn are somewhat more weakly related to this group. Another group includes some micro-components (Y, Nd, Ce, Rb, Th, V) with correlations exceeding 0.9 and Pb, Cd and Ga with correlations between 0.8 and 0.9. Correlation coefficients exceeding 0.8 are found between chloride, sulphate, Mo and As. Nitrate differs sharply from other species, having all correlations less than 0.4 by the absolute value, some of them negative. The results of the correlation analyses agree with groups from the cluster analysis. The factor analysis did not distinguish the fraction of fine particles, but shared the corresponding species between factor 1 and factor 2.

4.2.3. Deposition of metals

The application of statistical methods shows the presence of different transport and deposition mechanisms of atmospheric wastes from kukersite oil-shale

burning. Large particles with a diameter of several tens of micrometers containing Ca, for instance, are deposited closer to the source than small particles of a micrometer size order containing Pb. It is remarkable that all statistical methods used gave nearly the same groups of species interpreted as coarse and fine fly ash particles and gases from regional sources. Nitrate ion and Zn have powerful sources, though not related to oil-shale burning (road traffic, domestic heating, far transport), same kind of sources are detectable also for Cd, Pb and Cu. The groups of species discussed above are arbitrary, of course. All mineral components occur in all ash fractions. Many species are almost indifferent in regard to the ash fraction, and the transition between fractions is continuous. So, we can speak only about a few "typical" chemical species, representing each group.

Most of the trace metals have maximal loads at 10–15 km from the Estonian PP, the variations are relatively wide and the difference between woodland and open sites is not significant, which may refer to mixed dry and wet deposition.

4.3. Future directions

– Studying metal adsorption/desorption in very low concentrations when the concentration of metal ions in solution at equilibrium is in the range of ng/l or µg/l. Such concentrations are common in peat and soil.
– Using information-rich analysis. Nowadays simultaneous adsorption on an adsorbent of mainly just one or a few metals is studied. Using the ICP-MS or ICP-OES analysis technique on the other hand allows to study the adsorption/desorption of even about 70 metals under the same conditions, the only question being whether the investigator is willing to analyse the obtained data.
– Testing various adsorbents. Any adsorbent can be studied under the same conditions if a test scheme for adsorption experiments has been created.

5. CONCLUSIONS

A large amount of industrial wastewater containing various heavy metal ions is discharged annually by a number of industries. Pollution by heavy metals is an important environmental problem due to their toxicity and accumulation throughout the food chain. Although some metals are necessary for biological processes, all of them are toxic in high concentrations. Cadmium, lead, and nickel belong to the group of seriously hazardous heavy metals. Peat is a cheap adsorbent, which is abundant in nature, and which has a good ability to adsorb heavy metals. Multimetal competitive adsorption has extensively been studied by using various biosorbents, however, multimetal competitive adsorption onto peat has been described in only a few articles. Additionally, comparison of the available adsorption data is also difficult because of a great variety of peat types and metals used for adsorption tests.

The focus in the current investigation was on the choice of an adsorbent for leachate treatment and the adsorption of cadmium, lead and nickel ions from single- and multimetal solutions onto peat. Multimetal adsorption from spiked water solutions and spiked industrial landfill leachate solutions on different adsorbent materials was studied in batch tests. The results showed that the adsorbents based on peat are good adsorbents for heavy metal ions, having 3–10 times higher adsorption capacity than the other adsorbents investigated. For instance, the adsorption capacity was 10 times higher for peat than for semi-coke and three times higher than for pine bark. For a mixture of peat and carbon-containing ash, the difference was not so great (a factor of 1.3). Hence, peat combined with carbon-containing ash would also most probably be a good adsorbent for metals as well as for organic pollutants.

This work also investigates the multimetal competitive adsorption of three different metals onto highly decomposed, non-dried and non-pre-treated peat. Single- and multimetal adsorption of three metals onto the best adsorbent (peat A) was investigated to obtain more knowledge on competitive adsorption in more complex systems. The role of the desorption of calcium, magnesium and 9 other metals ions was evaluated. The results obtained from single-metal adsorption studies were used to show that maximum adsorption capacities decreased in the order of $Pb^{2+} > Cd^{2+} \geq Ni^{2+}$ in accordance with their decreasing ion radii of hydrated ions. An increase in the initial concentration of one metal ion in the solution decreases the amount of all other metal ions adsorbed from the solution onto Peat A. The change in the amount of Pb^{2+} adsorbed from the solution showed that Pb^{2+} has a much higher affinity to the adsorbent than the other two metal ions. The total concentrations of Cd, Ni and Pb ions adsorbed onto peat A were equal to the total concentrations of the desorbed Ca and Mg ions, strongly suggesting that exchangeable adsorption is one of most important processes taking place.

In addition, possibilities for modelling the adsorption process were investigated using the Langmuir adsorption isotherm and different linearizations of the isotherm. The use of the Langmuir equation for data modelling is necessary in

order to obtain constants for the equation. For data modelling, all four linear single-surface Langmuir isotherm transformations and one two-surface linear transformation could be used. It is also possible to compare the data found by means of linear regressions with the data obtained by non-linear regressions. Better results among linearizations were found with the Langmuir linearization, but the results obtained by using non-linear regression were still the best. The evaluation (using standard deviation and the correlation coefficients of regression) of the efficiency of different methods was performed, and more simplified and better data fitting calculation by non-linear regression for constants of the two-surface Langmuir isotherm were proposed.

The results of this study were planned to be applied in two ways. First, for developing a full scale treatment plant for leachate water, which aim was achieved completely. Second, for investigations of the deposition and adsorption/desorption onto peat and the humic-substance-rich forest soils of North-East Estonia. This aim was achieved partially, as the concentrations of metals in bog water are extremely low. During the investigations we were lacking good equipment for a statistically reliable detection of these concentrations. As ICP-MS nowadays is a very fast-developing technique, the corresponding equipment is in production already and was ordered by the author of the thesis. An interesting future prospect for the present study will be the investigating of metal adsorption/desorption at very low concentrations when the concentration of metal ions in the solution at the state of equilibrium is in the range of ng/l or µg/l.

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7. SUMMARY IN ESTONIAN

Cd^{2+}, Ni^{2+} ja Pb^{2+} koosadsorptsioon turbal

Keskkonna saastatus raskmetallidega on oluline probleem. Kuigi mõned uuritud metallidest võivad olla eluks vajalikud, on nad kõrgenenud kontsentratsioonide korral mürgised. Antud töös uuriti Cd^{2+}, Ni^{2+} ja Pb^{2+} koosadsorptsiooni turbal. Viimasel kümnendil on järjest rohkem hakatud uurima metallide samaaegset adsorptsiooni erinevatel adsorbentidel. Varem uuriti metallide adsorptsiooni lahusest üksikute metallide kaupa või ka mitut metalli sisaldavast lahusest, pööramata seejuures tähelepanu metallide konkureerivale adsorptsioonile. Nii looduslikus vees, kui ka heitvees on metallide konkureeriv adsorptsioon täiesti tavaline. Konkureeriva adsorptsiooni kohta turbal ja eriti looduslikul, töötlemata ja kõrge lagunemisastmega turbal on infot äärmiselt vähe.

Töö käigus katsetati nelja metalli koosadsorptsiooni tingimustes 8 erinevat adsorbenti. Katsete tulemusena ehitati ühe doktoriväitekirjas sisalduva artikli kaasautori poolt Rootsis kodumasinate prügila ja metallipurusti läbinud autoosade prügila heitvete puhasti. Kõige paremate omadustega adsorbendiga, nimetusega turvas A, tehti katsed ilma konkureeriva adsorptsioonita ja konkureeriva adsorptsiooni tingimustes. Leiti eelisadsorptsiooni rida järjestuses $Pb^{2+} > Cd^{2+} \geq Ni^{2+}$ ja põhjendati selle sõltuvust hüdratiseeritud iooni raadiusest. Leiti erinevate metallide maksimaalne adsorptsioonivõime turbal A. Erinevate metallide käitumist koosadsorptsiooni tingimustes hinnati pinna suhtelise täitumisastme ja metalli suhtelise adsorptsiooni kaudu. Vahetusadsorptsiooni hinnati turbalt desorbeerunud 11 metalli kontsentratsioonide järgi ning avastati, et niipalju kui Cd^{2+}, Ni^{2+} ja Pb^{2+} adsorbeerub, vabaneb ka turba pinnalt Ca^{2+} ja Mg^{2+}.

Uuriti ka protsessi modelleerimise võimalusi Langmuiri isotermi ja selle nelja teisenduse abil, võrreldi erinevaid võimalusi Langmuiri isotermi konstantide arvutamiseks ja koostati arvutamist lihtsustav matemaatiline mudel kaheosalise Langmuiri isotermi jaoks.

Täiendavalt uuriti 27 elemendi ja ühendi sadenemist turbale ja metsamuldadele Kirde-Eesti piirkonnas. Antud juhul sadenevad soojuselektrijaamadest ja tsemenditööstusest pärinevad leelismetallid, eelkõige kaltsium ja magneesium ja teised metallid ning raskmetallid koos mittemetallidega.

Eelnevatest uuringutest tulenev tulevikusuund oleks lisaks uute adsorbentide testimisele, ülimadalatel metallikontsentratsioonidel (ng/l või μg/l) toimuvate adsorptsiooniprotsesside uurimine. Lisaks veel metallide ning mittemetallide üheaegse adsorptsiooni/desorptsiooni uurimine, määrates reaalajas samaaegselt maksimaalne kogus metalle. Teoreetiliselt on induktiivsidestunud plasma aatomemissioonanalüüsil võimalik samaaegselt määrata üle 70 keemilise elemendi.

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PUBLICATIONS

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