

UNIVERSITY OF LATVIA
FACULTY OF GEOGRAPHY AND EARTH SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCE



Artis Robalds

**SORPTION OF THALLIUM(I), COPPER(II),
CHROMIUM(III) AND PHOSPHATE
BY PEAT BASED BIOSORBENTS**

SUMMARY OF DOCTORAL THESIS

Submitted for the degree of Doctor of Geography in Environmental Science,
Subfield of Environmental Protection

Scientific supervisor:
Professor, *Dr. habil. chem.* Māris Kļaviņš

Rīga, 2016

The research for doctoral thesis was carried out at the Department of Environmental Science, Faculty of Geography and Earth Sciences, University of Latvia, and it has been supported by the European Social Fund within the project “Support for Doctoral Studies at University of Latvia”, No. 2009/0138/1DP/1.1.2.1.2./09/IPIA/VIAA/004. Also support from ESF project “Interdisciplinary team of young scientists for research of bog resources, sustainable use and protection in Latvia (PuReST)”, No. 2014/0009/1DP/1.1.1.2.0/13/APIA/VIAA/044 is acknowledged.



IEGULDĪJUMS TAVĀ NĀKOTNĒ

Supervisor: Prof., *Dr. habil. chem.* **Māris Kļaviņš**, University of Latvia

Reviewers:

Prof., *Dr. sc. ing.* **Ritvars Sudārs**, Latvia University of Agriculture
Docent, *Dr. geogr.* **Raimonds Kasparinskis**, University of Latvia
Leading researcher, *Dr. chem.* **Sarma Valtere**, Riga Technical University

The thesis will be defended at a public session of the Doctoral Committee of Environmental Science, University of Latvia, at the Faculty of Geography and Earth Sciences of the University of Latvia (1 Jelgavas Street, Riga, Latvia) on January 22, 2016 at 10:00.

The thesis is available at the Library of the University of Latvia (19 Raiņa Blvd, Riga, Latvia).

Chairman of the Doctoral Committee:

Prof., *Dr. biol.* **Viesturs Melecis**, University of Latvia

Promotion Council:

Prof., *Dr. geogr.* **Olģerts Nikodemus**, University of Latvia
Assoc. prof., *Dr. biol.* **Gunta Sprinģe**, University of Latvia
Prof., *Dr. habil. chem.* **Māris Kļaviņš**, University of Latvia
Assoc. prof., *Dr. geogr.* **Laimdota Kalniņa**, University of Latvia
Dr. geogr. **Juris Burlakovs**, Linnaeus University, Sweden

© University of Latvia, 2016

© Artis Robalds, 2016

ANNOTATION

The possibilities to use peat biosorbents for the treatment of waters polluted with thallium(I), copper (II), chromium (III) ions, as well as phosphate ions have been studied in doctoral thesis. During the studies, the sorption efficiency of peat biosorbents have been determined depending on the physicochemical properties of peat, as well as on a number of environmental parameters such as, the temperature, pH and ionic strength of the solution. Results shows that peat obtained in Latvia can be used as an effective adsorbent for the binding of thallium(I), copper(II) and chromium(III) ions. The sorption efficiency of raw peat towards phosphates was relatively low, therefore, in order to improve sorption efficiency, peat was modified by iron compounds. Modified peat adsorbed phosphates with high efficiency not only using synthesized solution, but also phosphates from wastewater samples.

Keywords: adsorption, biosorption, phosphates, peat, heavy metals

CONTENT

Introduction	5
1. Literature review	9
1.1. Peat as biosorbent	9
1.2. Peat as biosorbent for the removal of heavy metals and mechanisms controlling metal biosorption	9
1.3. The practical use of peat biosorbents	10
2. MATERIALS AND METHODS	12
2.1. Materials	12
2.2. Sorption experiments	13
3. RESULTS AND DISCUSSION	14
3.1. Sorption of thallium(I) ions by peat	14
3.1.1. Characteristics of the peat	14
3.1.2. The effect of experimental parameters	15
3.1.3. Sorption performance of different peat types	17
3.2. Sorption of copper(II) and chromium(III) ions by peat	18
3.2.1. Sorption isotherms of Cu(II) ions	18
3.2.2. The impact of environmental parameters on the sorption character	21
3.3. Removal of phosphates by peat modified with iron hydroxide	22
3.3.1. Characteristics of the sorbents	22
3.3.2. Removal of phosphate from synthetic solutions	24
3.3.3. Removal of phosphate from wastewater	28
3.3.4. Recycling of spent sorbent	29
CONCLUSIONS	31
REFERENCES	32

INTRODUCTION

New solutions for the treatment of wastewater should be proposed, as traditional wastewater treatment methods have a number of serious shortcomings. For example, they are not sufficiently effective if there is a low concentration of the pollutant in the solution, there is a need for a large reagent and energy consumption, and toxic sludge and other wastes are formed (Volesky and Naja, 2005; Cochrane et al., 2006; Sen Gupta et al., 2009). Therefore there is a need to use new methods that would be inexpensive, but at the same time efficient and environmentally friendly.

The use of biosorbents to bind or adsorb pollutants meets the mentioned conditions, therefore the research of biosorption is an integral part in research areas, which are focused on how to find the best solutions to treat polluted waters as well as in other areas for the recultivation of the environment. The large number of studies (about 3500 publications with a word "*biosorption*" or "*biosorbent*" in the title; 2004–2014; the Scopus database) confirms the importance of the problem and shows that a wide range of scientists are involved in the search for the most efficient solution.

Many studies are devoted to finding suitable biosorbents for the removal of heavy metal ions since it is known that many of these metal ions are toxic in low concentrations, are not biodegradable, and are carcinogenic (Volesky and Naja, 2005; Cojocaru et al., 2009). In turn, peat is one of the most appropriate biosorbent for the biosorption of heavy metals because peat is a material with unique properties: large specific surface area; high water-holding capacity and high porosity; it is easy to handle, process, grade and blend; it is widely available in many parts of the world and is a relatively cheap material (Ho et al., 1995; Dean and Tobin, 1999; Joosten and Clarke, 2002; Rasmussen et al., 2002; Ringqvist et al., 2002).

A significant group of pollutants are phosphorus compounds and excessive amounts of these compounds in surface waters can lead to the eutrophication; a serious environmental problem in many countries around the world. Eutrophication causes depletion of oxygen, blooms of toxic algae, and degradation of water quality (Zeng et al., 2004; Song et al., 2011). Many studies have been devoted to finding the best solution in order to reduce the mentioned problems. Studies show that the use of biosorbents could be one of the best options to treat phosphate rich waters. While peat can be used for the removal of phosphate ions from aqueous solutions (Xiong and Mahmood, 2010), the sorption capacity of raw peat is low. Therefore, we need to find a way to increase the sorption capacity of peat towards phosphate ions.

The aim of the thesis is to investigate the possibilities of using peat and its modification products for the sorption of thallium(I), copper(II), chromium(III) and phosphate ions.

The main tasks of the thesis:

1. To collect and evaluate information about the use of peat biosorbents in the treatment of polluted waters.
2. To collect and evaluate information about mechanisms controlling biosorption and approaches for grouping these mechanisms.
3. To study thallium(I), copper (II) and chromium(III) ion sorption on peat samples; to characterize sorption kinetics, factors influencing sorption, and to describe sorption mechanisms.
4. To investigate the sorption of phosphates on peat modified with iron hydroxide; to determine the factors influencing sorption capacity; to characterize the developed sorbent.
5. To evaluate the phytotoxicity of the spent sorbent (peat modified with iron hydroxide).

Theses to be defended:

- The peats ability to bind thallium(I), copper(II) and chromium(III) ions is influenced by pH and temperature of the solution, contact time between the sorbent and the sorbate.
- By modifying peat with iron hydroxide, it is possible to substantially increase the peats sorption capacity towards phosphate ions.

Scientific novelty of the study:

- For the first time, study where peat has been used as a biosorbent for the removal of thallium(I) ions has been conducted.
- The possibilities to use the bog peat to bind chromium(III) and copper(II) ions have been investigated. The sorption mechanisms, as well as the limiting factors have been described.
- By modifying bog peat with iron hydroxide, a new sorbent has been developed, which demonstrates a high ability to bind phosphates. Possibilities to utilize the phosphate saturated peat have been proposed.

The theoretical and practical importance of the work

- It has been proved that bog and fen peat obtained in Latvia can be used as effective biosorbents to bind heavy metal ions.
- A new sorbent has been developed, which can be used to reduce the concentration of phosphates in municipal wastewater.
- For the first time, information on mechanism controlling biosorption has been summarized.

Approbation of the results

The results of the doctoral thesis have been discussed and summarized in 7 scientific publications, 8 international scientific conferences and 7 local scientific conferences in Latvia.

Scientific publications:

1. **Robalds, A.**, Gaja, G.M., Klavins, M. (2016) Highlighting inconsistencies regarding metal biosorption. *Journal of Hazardous Materials*, 304, 553-556.
2. **Robalds, A.**, Dreijalte, L., Bikovens, O., Klavins, M. (2015) A novel peat-based biosorbent for the removal of phosphate from synthetic and real wastewater and possible utilization of spent sorbent in land application. *Desalination and Water Treatment*. Published online.
3. Krumins, J., **Robalds, A.** (2014) Biosorption of metallic elements onto fen peat. *Environmental and Climate Technologies*, 14, 12-17.
4. **Robalds, A.**, Klavins, M., Dreijalte, L. (2013) Sorption of thallium(I) ions by peat. *Water Science and Technology*, 68(10), 2208-2213.
5. Krūmiņš, J., **Robalds, A.**, Purmalis, O., Ansonē, L., Poršņovs, D., Kļaviņš, M., Segliņš, V. (2013). Kūdras resursi un to izmantošanas iespējas. *Materiālzinātne un lietišķā ķīmija*, 29(1), 82-94.
6. Klavins, M., Porshnov, D., Ansonē, L., **Robalds, A.**, Dreijalte L. (2012) Peat as natural and industrial sorbent. In: R.A.R. Ramos, I. Straupe, T. Panagopoulos (Eds.), *Recent Researches in Environment, Energy Systems & Sustainability* (pp. 146-151). Faro, Portugal: WSEAS Press.
7. **Robalds, A.**, Klavins, M., Zicmanis, A. (2011) Peat as sorbent for Cu²⁺ and Cr³⁺ Ions. *Latvian Journal of Chemistry*, 50(1/2), 149-158

Patent:

Robalds, A., Dreijalte, L., Ansonē, L., Kļaviņš, M. (2012) Sorbent for purifying water from phosphorous compounds. Latvian Patent No. 14518 A. SPK kl. B01J20/06; C02F1/28. 20.05.2012.

Reports presented at the international conferences:

1. **Robalds, A.**, Klavins, M., Dreijalte, L. (2012) Removal of phosphate from aqueous solution by iron modified peat. In: *Proceedings of the 13th international conference Wetland systems for water pollution control (Volume II)* (pp. 264-271). Perth, Australia: International Water Association.
2. **Robalds, A.**, Klavins, M., Dreijalte, L. (2012) Sorption of Thallium(I) ions from aqueous solution by peat. In: *Book of abstracts of the 17th international scientific conference "Ecobalt 2012"* (p. 70). Riga, Latvia: University of Latvia Press.
3. **Robalds, A.**, Dreijalte L., Klavins M. (2012) Peat as sorbent for the removal of phosphate ions from aqueous solution. In: *Proceedings of the 14th International Peat Congress (Volume IV)* (pp. 140-143). Stockholm, Sweden: International Peat Society.
4. Kļaviņš, M., Porshnov, D., Ansonē, L., **Robalds, A.**, Dreijalte, L. (2011) Innovative use of peat: peat as sorbent. In: *Program and abstract book of Baltic countries peat producers forum* (pp. 20-22). Riga, Latvia: Latvian Peat Producers Association.
5. **Robalds, A.**, Klavins, M., Purmalis, O. (2011) Sorption of copper and chromium onto peat. In: *Abstract book and field session guide of the 9th International Conference*

Humic substances in ecosystems (HSE9) (p. 87). Karpacz, Poland: International Humic Substances Society.

6. Klavins M., Purmalis O., Porshnov D., Ansonē L., **Robalds A.**, Silamikele I. (2011) Peat and their humic matter properties and new areas of application. In: *Proceedings of Workshop Peat and humic substances „Current research in chemical, physical and biological characterization of peat”* (pp. 5-8). Zittau, Germany: International Peat Society.
7. Eglīte, L., Kļaviņš, M., **Robalds, A.**, Purmalis, O., Zicmanis, A. (2009) Peat collected from Latvia peat bogs as sorbents for trace elements. In: *Abstract book of SETAC Europe annual meeting. Protecting ecosystem health: facing the challenge of a globally changing environment* (p. 94). Göteborg, Sweden: SETAC Europe Office.
8. Kļaviņš, M., Eglīte, L., **Robalds, A.**, Frisk, T. (2008) Peat and its modification products as sorbents for trace elements. In: C. Farrell, J. Feehan (Eds.), *Proceedings of the 13th International Peat Congress (Volume II)* (pp. 121-123). Tullamore, Ireland: International Peat Society.

Acknowledgements

I express my gratitude to the scientific supervisor of my thesis – professor *Dr. habil. chem.* Māris Kļaviņš for the consultation, advice, support of new ideas, as well as the warm attitude during the research work. I would like to thank all my colleagues, especially Linda Ansonē-Bērtiņa and Līga Dreijalte for the fruitful discussions, as well as Jānis Krūmiņš for the valuable comments on the thesis. I would like to thank *Silu kudra Ltd.* (Latvia) for the possibility to obtain peat samples for my studies.

I would like to express my sincere gratitude to all of my family especially Ieva, Adrians and Hanna Amanda for the love, support, encouragement, and understanding in the times when there was no opportunity to be with them as much as they would like. Special thanks to Niāra Robalde whose care, upbringing and support has created a strong base for the results I have achieved.

1. LITERATURE REVIEW

1.1. Peat as biosorbent

Activated carbon is widely used in the treatment of polluted waters. However, studies have shown that activated carbon can be replaced by adsorbents of biological origin or so-called biosorbents whose usage costs are significantly lower. Peat is one of the most studied biosorbent (Gupta et al., 2009; Wang and Chen, 2009), which has been used in the biosorption studies at least from the 1960s (Ho and McKay, 2004). According to Kuziol and coworkers, peat is the most appropriate material to study factors affecting the organic material's ability to bind metal ions, as well as to study what is the sorption mechanism (Kuziol et al., 2006). Peat is used to clean wastewater from heavy metal ions, such as copper, zinc, cadmium, and chromium (Ringqvist and Osborne, 2002; Qin et al., 2006), dyes (Ho and McKay, 1998), phosphorus and nitrogen compounds (Xiong and Mahmood, 2010), and various organic substances, such as polycyclic aromatic hydrocarbons (Rasmussen et al., 2002; Ringqvist et al., 2002). The large number of studies have been conducted because peat has unique characteristics: large specific surface area; high water-holding capacity, and high porosity; it is easy to handle, process, grade and blend; it is widely available in many parts of the world and is relatively cheap (Ho et al., 1995; Dean and Tobin, 1999; Joosten and Clarke, 2002; Rasmussen et al., 2002; Ringqvist et al., 2002).

1.2. Peat as biosorbent for the removal of heavy metals and mechanisms controlling metal biosorption

Traditional wastewater treatment methods or some of the most commonly used methods to reduce the concentration of metal ions in aqueous solutions are: chemical precipitation, ion exchange, oxidation/ reduction methods, reverse osmosis, and solvent extraction. Ion exchange and chemical precipitation are used at the industrial level as these processes are predictable and well understood (Gadd, 2009). The main disadvantages of the traditional treatment methods are that they: 1) can not be used if there is a low concentration of metal ions in the solution, i.e., they are not cost-effective enough as other methods when there is a low concentration of metal ions in the solution; 2) have high consumption of energy and reagents; 3) have a high production of toxic sludge and other waste (McKay and Porter, 1997; Volesky and Naja, 2005; Cochrane et al., 2006; Sen Gupta et al., 2009). These shortcomings are often used as a basis for the arguments of why it is necessary to use biosorbents, and why biosorption should be offered as an alternative or complement to traditional treatment methods (Gadd, 2009). Most of the biosorption studies (where peat is used as a biosorbent) are devoted to study the sorption of the heavy

metal ions (for example, Dean and Tobin, 1999; Ho and McKay, 2003; Gundogan et al., 2004; Cochrane et al., 2006; Kalmykova et al., 2008; Batista et al., 2009; Cerqueira et al., 2012). Physical and chemical properties of peat (for example, a high cation exchange capacity) provides a high sorption capacity of peat towards heavy metal ions (Ringqvist and Osborne, 2002).

It is widely discussed what the mechanisms controlling metal sorption on peat are, and it should be emphasized that various studies have given different results. Ion exchange, complexation, as well as physical adsorption are considered to be the most important mechanisms (Brown et al., 2000). Since several mechanisms can be involved as well as it being difficult to determine the exact removal mechanism, the general term “*sorption*” is often used (Ho and McKay, 2004). Research shows that the peat forming moss species such as *Sphagnum fuscum* and *Sphagnum balticum* can bind metals by physical adsorption, ion exchange and chelation (Onianwa, 2001). Several mechanisms may provide peat the ability to bind heavy metals, but these processes can take place in parallel in different combinations, therefore the identification of the biosorption mechanisms are not always simple (Chong and Volesky, 1995). For example, Asapo (2011) found that at lower pH values complexation predominantly takes place while at higher pH values ion exchange reactions were favored. If the wastewater treatment takes place in constructed wetlands then not only do the above mentioned processes take place, but also other biological, chemical and physical processes ensure wastewater treatment. These processes are suspended metal filtration, bioaccumulation of metals and metal sulphide precipitation (Frostman, 1993). Although information about factors influencing metal sorption can be found in previous studies, there are authors who point out that it is not fully understood what the mechanisms controlling sorption of metal ions by biosorbents are, including peat (McKay and Porter, 1997; Ringqvist et al., 2002; Kyziol et al., 2006). Therefore one could conclude additional studies are needed to determine peats effectiveness as a heavy metal biosorbent.

1.3. The practical use of peat biosorbents

Most of the experiments where peat sorption properties have been evaluated are carried out in laboratory conditions using an approach called “*batch sorption experiments*” (also called “*batch-type tests*”, “*batch tests*” or “*batch studies*”). When this approach is used, peat is mixed (usually for 24 h) with a solution containing a pollutant, which is followed by separating peat from the solution by filtration or centrifugation. After filtration, in order to calculate the sorption capacity of peat, the concentration of the adsorbate is calculated in the initial solution, as well as in the filtrate. This approach is fast and simple, but it gives only a rough idea of whether the studied adsorbent could be used in real wastewater treatment systems. Thus it is necessary to carry out studies where peat has been used in “*full-scale systems*”. One of the possible solutions to use peat practically in wastewater treatment could be its use as a material in constructed wetlands. For example, in a study by Svensson et al., in 2011, peat was mixed with carbon-containing ash, and the mixture was used to treat wastewater from professional car washes, landfill leachate and stormwater. This mixture was capable to simultaneously remove both inorganic and

organic pollutants. Another study (Mayes et al., 2009) indicated that strongly mineralized peat used in constructed wetland provided a pH decrease of alkaline waters. Increased pH of the solution formed in the first stage of the wastewater treatment as oil shale (alkaline material) was used. If a construction of constructed wetland is not necessary or possible, then the peat can also be used in more simple way – peat is inserted into the container through which the wastewater is filtered (Rentz et al., 2009). Peat in the treatment of wastewater can also be used in environments where peat is found naturally – in bogs and fens. Untreated or partially treated wastewater is entered into the peatlands, which act as a biofilter. However, such practice is considered to be environmentally unfriendly, so it is used less often.

2. MATERIALS AND METHODS

2.1. Materials

Sorption of Tl(I), Cu(II), Cr(III) or phosphate ions on peat and modified peat was studied by using peat samples collected from several bogs and fens in Latvia (Figure 2.1.1.). After the sampling, peat samples were wrapped in polyethylene film and delivered to the laboratory.

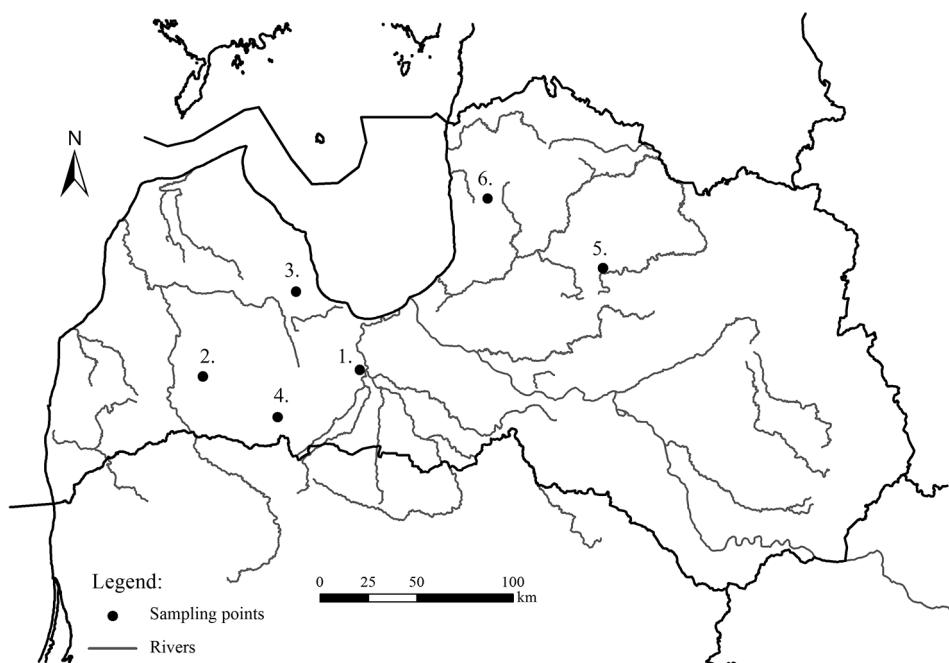


Figure 2.1.1. Sampling points: 1. Kaigu bog; 2. Mazais Veikēnieku bog; 3. Siļu bog; 4. Viķu mire; 5. Taurenē mire; 6. Svētupes mire

Prior to the sorption experiments, peat samples were homogenized, air dried, then dried at 105 °C for 24 h (using Gallenkamp Plus II Oven), sieved through a 2 mm sieve to remove large particles, and finally placed in sealed polythene bags for future use. The modified peat for the removal of phosphates was prepared using an approach similar to that of Harvey and Rhue (2008): 67.55 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 250 mL of distilled water, then 250 mL of 3.0 M NaOH was added, and the suspension was left for

4 hours. The precipitate was then thoroughly mixed with 100 g of peat (Siřu 12.5–25 cm), left overnight (16 h), filtered, washed with 250 mL deionized water, air-dried and heated for 4 hours at 60 °C.

The following parameters of raw and modified peat were determined: botanical composition, peat type, degree of decomposition (Silamiřele, 2010); dry weight and moisture content (according to the ISO 11465 standard); pH value (according to the ISO 10390 standard); cation exchange capacity (according to the ISO 11260 standard); content of organic matter (according to Heiri et al., 2001). Elemental analysis was performed by using a Carlo Erba EA 1108 Elemental Analyzer. The point of zero charge (pH_{ZPC}) was measured by the pH drift method (according to Fiola and Villaescus, 2009). Total concentrations of metals in the peat, modified peat and spent sorbent were analyzed using an atomic absorption spectrometer (PerkinElmer AAnalyst 200) after nitric acid digestion (according to the EPA Method 3050B). The particle-size distribution of peat and modified peat was analyzed by the conventional dry-sieving technique. The FTIR spectra were acquired in KBr pellets (using a Perkin Elmer Spectrum BX FT-IR). X-ray diffraction (XRD) analysis of modified peat was conducted with a Bruker D8 Advance X-Ray powder diffractometer employing CuK_α radiation. The specific surface areas of raw and modified peats were estimated by the Brunauer-Emmett-Teller (BET) method, using a surface area analyzer (Gemini 2360).

2.2. Sorption experiments

The sorption of Tl(I), Cu(II), Cr(III) or phosphate ions onto peat and modified peat was studied by batch experiments with varying initial Tl(I), Cu(II), Cr(III) or phosphate ion concentration, pH, contact time, ionic strength and temperature. The experiments were conducted as follows: 1.0 g of peat (or modified peat) was mixed with 80 mL of aqueous solution containing Tl(I), Cu(II), Cr(III) or phosphate ions using capped bottles (100 mL). Samples were shaken on a rotary shaker with a constant speed of 140 rpm for 24 h. The suspensions were filtered and the concentration of Tl(I), Cu(II), Cr(III) ions in the filtrates as well as in the initial solutions was determined by PerkinElmer AAnalyst 200 atomic absorption spectrometer (AAS). The phosphate content in the filtrates, initial solutions and wastewater was determined by the molybdenum blue spectrophotometric method at λ_{max} of 880 nm (Murphy and Riley, 1962) using a Hach Lange DR 2800 spectrophotometer. In the pH studies, the initial pH values of metal solutions were in the range 2–10, which were adjusted using 1.0 N, 0.5 N and 0.1 N HCl or NaOH with a pH meter (HANNA instruments pH 213) before the addition of the peat or modified peat.

3. RESULTS AND DISCUSSION

3.1. Sorption of thallium(I) ions by peat

3.1.1. Characteristics of the peat

Fen peat from Taurene transitional mire was used in this study and its characteristics are given in table 3.1.1. Peat is characterized by relatively low concentration of organic matter, high degree of decomposition, high pH value and concentration of the exchange cations. Fen peat was used in this study, as the results of the preliminary study showed that the sorption capacity of this sample is significantly higher than that of bog peat samples.

Table 3.1.1.

Characteristics of studied peat

Parameter				Value			Concentration of metals; mg/kg	
Peat type				Wood-grass peat			Na	57
pH (in H ₂ O)				6,35			Mg	2098
Organic matter, %				81			K	633
Degree of decomposition, %				53			Ca	13386
pH _{ZPC}				6.20			Fe	7942
C, %				52.94			Cr	13,8
H, %				4.96			Mn	207
N, %				1.79			Ni	9.9
Exchangeable ions, cmol/kg							Cu	12.4
							Zn	10.1
Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Al ³⁺	Fe ³⁺	Mn ²⁺	Cd	0.440
56	13.3	0.099	0.107	0.009	0.007	0.029	Pb	9.6

The determination of the physicochemical parameters is needed, because it may help to explain the nature of the sorption in relation to the specific sorbate. For example, studies have shown that the sorption capacity of thallium(I) ions in the soil are ensured by ion exchange reactions (Jacobson et al., 2005).

3.1.2. The effect of experimental parameters

Effect of initial Tl(I) concentration and temperature

The effect of initial Tl(I) concentration, as well as the effect of temperature is presented in Figure 3.1.1. The sorption capacity of peat increased with initial Tl(I) concentration for all temperatures studied. However, equilibrium was not reached and thus further increase of the initial Tl(I) concentration would result in increase of sorption capacity. At 20 °C, the absolute amount of Tl(I) ions sorbed per unit of peat increased from 0.04 to 24.14 mg/g with increase of initial Tl(I) ion concentration from 1 to 500 mg/L. However, the percentage removal decreased from 84.3 to 62.3 %. Observed sorption capacity was strongly dependent on temperature. The amount of Tl(I) ions sorbed per unit of sorbent increased from 20.87 mg/g (55.9 % removal) to 25.18 mg/g (67.2 % removal) when temperature decreased from 40 to 2 °C. The decrease of sorption effectiveness caused by increased temperature indicated the exothermic nature of the sorption process.

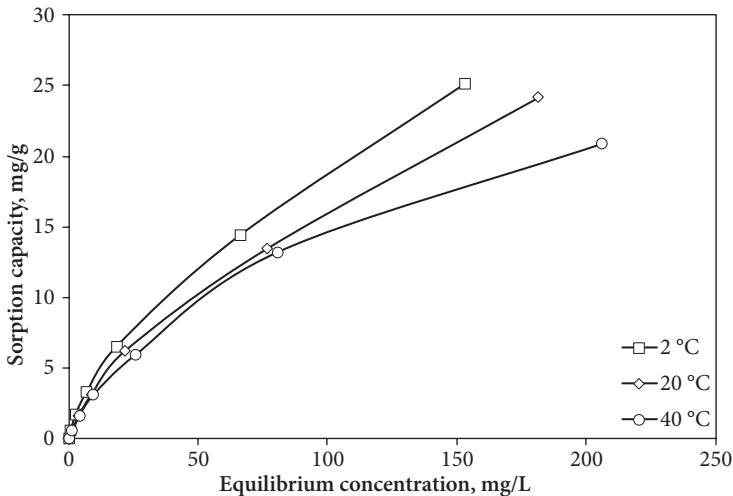


Figure 3.1.1. Effect of initial concentration and temperature on the sorption of Tl(I) ions by peat ($m = 1.0$ g; $V = 80$ mL of 10 mg/L Tl(I); $t = 24$ h)

It must be pointed out that sorption capacity is not the only parameter determining suitability of a sorbent for use in large-scale field systems, such as constructed wetlands. Content of heavy metals, availability of the biosorbent, hydraulic conductivity and other parameters should be taken into consideration as well (Vohla et al., 2011).

Effect of contact time

When tested material is being evaluated as a potential sorbent in a fixed bed or any other type of flow through system, kinetic performance is the most important data to be

considered (Qiu et al., 2009). Sorption kinetics helps to determine the time necessary for the system to reach equilibrium, i.e., the point when there is no change of sorbate concentration in the solution. The kinetics of the sorption process appears to be a two stage process. In the first stage the removal is very rapid – 82.8 % of Tl(I) ions were sorbed within the first 10 minutes. The first stage was followed by a slower uptake of Tl(I) ions. Equilibrium was reached (curve became horizontal) in 25 minutes with 86.3 % (0.69 mg/g) sorbed. Qin and coworkers (2006) reported previous findings from Aringhieri's group (1985), who initially linked the first rapid stage with diffusion of metal ions from solution to the external adsorbent surface. They observed slower uptake in the second stage, which was linked to the diffusion into the porous structure of the sorbent. The results are similar with that of Memon and coworkers (2008) where other biosorbent (sawdust) was used for the sorption of Tl(I) ions. In that study, equilibrium was reached in less than 10 minutes.

Data from the batch kinetic studies on sorption of Tl(I) on peat were analyzed using the pseudo-first order and pseudo-second order kinetic models (Lagergren, 1898; Ho and McKay, 1998; Ho and McKay, 2004). Both of these models have been used in various studies to describe the mechanism of sorption in peat/metal systems (Cochrane et al., 2006; Qin et al., 2006; Kalmykova et al., 2008). Calculated coefficients of determination for the pseudo-first order and pseudo-second order reactions were 0.819 and 0.999, respectively, indicating that the pseudo-second order model is better in terms of describing the sorption process. That suggests that the chemisorption process could be the rate-limiting step, involving valence forces or covalent forces between the sorbent and the sorbate (Ho and McKay, 2000). Peat components, especially lignin, contain functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxyls and ethers, which may serve as potential chemical bonding agents (Ho and McKay, 2004).

Effect of pH

The pH values during the sorption changed significantly from the initial pH of the solution, indicating a strong buffer capacity of peat. In the experiments pH after 24 h changed from initial values of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 to 4.08, 5.56, 5.89, 6.08, 6.16, 6.21, 6.25, 6.28, and 6.33, respectively. The decrease of pH can be attributed to the displacement of protons (H^+) from peat by heavy metal ions (Twardowska et al., 1999; Sun et al., 2004). The change of pH can also be caused by the buffering behavior of peat. Peat contains humic acids as one of its major components (Ho and McKay, 1998) and it can be assumed these humic acids are responsible for this buffer capacity. Pertusatti and Prado (2007) reported that humic acids have a significant buffer capacity in a wide pH range. In view of the buffering capacity of the peat, in other experiments, pH of the solution was adjusted during the sorption process. The uptake of Tl(I) gradually increased as pH was increased from 2.0 to 10.0. The maximum sorption capacity occurred at pH 10 with sorption capacity of 0.82 mg/g (97.6 % removal) (Figure 3.1.3).

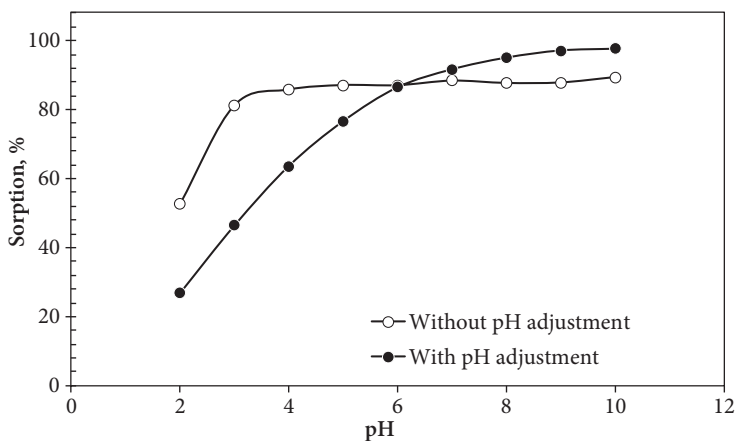


Figure 3.1.3. Effect of pH on the uptake of Tl(I) ions by peat ($m = 1.0$ g; $V = 80$ mL of 10 mg/L Tl(I); $t = 24$ h; $T = 20$ °C)

These results are in good agreement with the well-known explanation of competition between hydrogen ions and ions of metal in the solution. At lower pH values hydrogen ions compete with metal ions for adsorption sites in the sorbent. When the pH of the solution is increased, the hydrogen ion concentration in the solution decreases and as a result an increase of metal uptake is observed.

Effect of ionic strength

The increase of ionic strength caused a decrease of Tl(I) sorption capacity, indicating that the treatment with K^+ and Cl^- ions had a significant influence on sorption of Tl(I) ions. When the ionic strength was set to 0.05; 0.10; 0.25; 0.50; 0.75 and 1.0 mol/L, the sorption capacity was 0.54; 0.49; 0.38; 0.30; 0.25 and 0.20 mg/g, respectively (data not shown). According to literature, monovalent Group I cations can compete for reactive sites with Tl(I) ions (Sangvanich et al., 2010).

3.1.3. Sorption performance of different peat types

In order to demonstrate that peat samples obtained from other geographical locations could be used as effective Tl(I) biosorbents, sorption capacities of six different peat samples have been determined. Table 3.1.2. shows Tl(I) sorption capacity, as well as major physicochemical properties of the chosen peat samples.

Table 3.1.2.

Sorption performance of different peat samples

	Taurenes transitional mire 375–400 cm	Viķu mire 75–100 cm	Svētupes mire 130–150 cm	Kaigu 45–70 cm	Sīļu bog 12,5–25 cm
Peat type	Wood-grass peat		Sedge peat	<i>Sphagnum fuscum peat</i>	<i>Sphagnum-cotton grass peat</i>
Degree of decomposition, %	53	38	34	10	27
pH (in H ₂ O)	6.35	5.78	5.68	3.91	3.31
Organic matter, %	81	91	88	99	97
	Tl(I) sorption capacity; mg/g				
	15.1	11.9	14.0	10.4	8.5

The results show that sorption capacity is relatively high, regardless of the type of peat used. Further investigation would be recommended to develop a better understanding about peat properties that control the sorption process.

3.2. Sorption of copper(II) and chromium(III) ions by peat

3.2.1. Sorption isotherms of Cu(II) ions

To determine the ability of peat to adsorb copper(II) ions, peat samples with different physical and chemical properties were used (Table 3.2.1.). Altogether 7 peat samples were used, and they were collected from Kaigu bog (4 samples) and Mazais Veikēnieks bog (3 samples).

The sorption isotherms (Figure 3.2.1.) shows that the maximum sorption capacity of copper (II) ions of the studied peat samples are relatively similar. The studied peat samples can be divided into two groups. In the first group, there are peat samples with the lowest sorption capacity: Kaigu 0–25 cm, Kaigu 95–125 cm, Mazais Veikēnieks 0–30 cm. It was observed that the sorption capacity of peat samples collected from Mazais Veikēnieks 30–60 cm, Mazais Veikēnieks 60–90 cm and Kaigu 45–70 cm are not statistically different – about 12 mg/g. The concentration of copper(II) ions in the wastewater can reach 25 mg/L, thus it is necessary to determine the sorption efficiency at this concentration (Cojocar et al., 2009). All the peat samples showed high sorption efficiency – it was observed that the sorption efficiency towards Cu(II) ions reached 81.7 % (Mazais Veikēnieks 30–60 cm) to 95.3 % (Kaigu 125–145 cm).

Table 3.2.1.

Characteristics of studied peat samples

Peat sample	M.V.* 0–30 cm	M.V.* 30–60 cm	M.V.* 60–90 cm	Kaigu bog 0–25 cm	Kaigu bog 45–70 cm	Kaigu bog 95–125 cm	Kaigu bog 125–145 cm
Peat type	<i>Sphagnum fuscum</i> peat	Magellan's <i>Sphagnum</i> peat	Wood-grass peat	Cotton grass- <i>Sphagnum</i> peat	<i>Sphagnum fuscum</i> peat	Narrow-leaf <i>Sphagnum</i> peat	<i>Sphagnum fuscum</i> peat
Decomposition degree, %	15	10	8	9	10	31	24
Ash content, %	1.08	1.30	2.32	3.26	0.77	0.66	0.86
S, %	0.69	0.54	1.08	0.69	0.77	0.72	0.67
C, %	45.67	46.49	52.46	48.26	49.56	48.54	41.75
H, %	5.65	5.80	6.15	5.76	5.71	5.59	4.96
O, %	46.87	45.87	37.19	41.57	43.16	44.44	51.73
N, %	0.73	0.53	1.88	1.15	0.80	0.78	0.70
pH _{KCl}	3.01	3.14	3.66	3.02	3.11	3.26	3.31

* Bog Mazais Veikēnieks

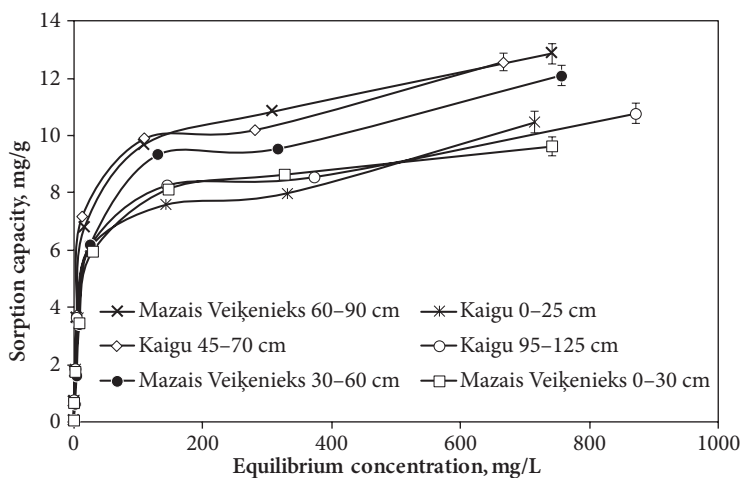


Figure 3.2.1. Sorption isotherms (Cu(II)) of different peat samples
($m = 1.0$ g; $V = 80$ mL; $T = 20$ °C; $t = 24$ h)

In order to determine maximum sorption capacity of peat samples, the Langmuir theoretical sorption model or equation was used (Mohan and Pittman, 2006). Table 3.2.2. shows the sorption capacity determined in this study, the maximum sorption capacity calculated by the model and the constant b , which shows the force between the sorbent and the sorbate – a higher value of b indicates a lower affinity (Kratochvil and Volesky, 1998).

Table 3.2.2.

Sorption capacity of peat samples used in this study and parameters of mathematical models

Peat sample	Actual (experimental) sorption capacity, mg/g	Langmuir equation			Freundlich equation
		Sorption capacity q_m , mg/g	Constant b	r^2	r^2
M.V.* 0–30 cm	9.61	9.78	0.0434	0.999	0.849
M.V.* 30–60 cm	12.09	12.40	0.0269	0.995	0.881
M.V.* 60–90 cm	12.86	13.04	0.0378	0.996	0.836
Kaigu bog 0–25 cm	10.45	10.25	0.0416	0.983	0.853
Kaigu bog 45–70 cm	12.56	12.51	0.0548	0.996	0.855
Kaigu bog 95–125 cm	10.76	10.67	0.0407	0.990	0.820

* Bog Mazais Veikšenieks

Results show that the sorption capacity of peat samples used in this work are comparable to that of peat samples used in other studies: *Sphagnum* peat from Canada – 16.1 mg/g (Gardea-Torresdey et al., 1996), grass peat from Turkey – 3.53 mg/g (Gundogan et al., 2004), *Sphagnum* peat from Ireland – 14.3 mg/g (Ho and McKay, 2003).

The same peat samples used for the removal of copper(II) ions were used for the removal of chromium(III) ions. For comparison, a fen peat from Taurenas mire was used. Peat samples from Kaigu bog and also from Mazais Veikšenieks bog showed equally high sorption capacity, therefore only one sample of each bog is shown (Figure 3.2.2.). Results showed that the peat sample from Taurenas mire had a significantly higher sorption – the maximum sorption capacity reached 27.8 mg/g, approximately 3 times higher than the maximum sorption capacity of the peat samples from Kaigu bog and Mazais Veikšenieks bog.

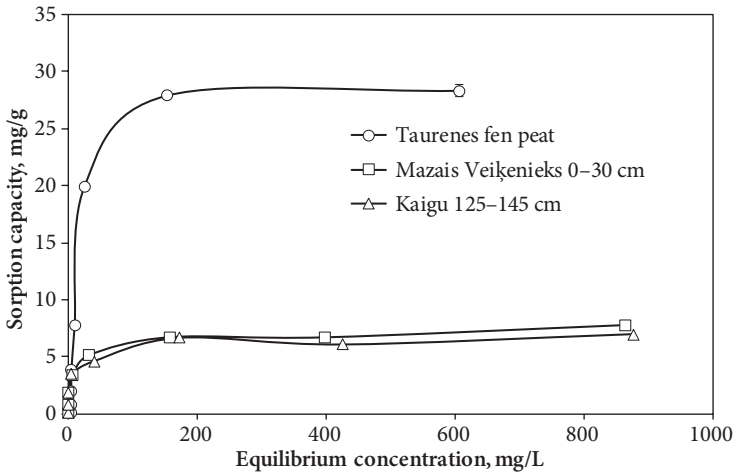


Figure 3.2.2. Sorption isotherms (Cr(III)) of different peat samples ($m = 1,0$ g; $V = 80$ mL; $T = 20$ °C; $t = 24$ h)

The high difference in the sorption capacity is most likely due to the fact that the peat sample from Taurenes mire had a significantly higher pH value compared to other peat samples. The $\text{pH}_{\text{H}_2\text{O}}$ of the peat sample from Taurenes mire was 6.35, but the pH_{KCl} of the peat samples from Kaigu bog and Mazais Veikēnieks bog were 3.26 and 3.66, respectively.

3.2.2. The impact of environmental parameters on the sorption character

The effect of contact time

The adsorption of copper(II) and chromium(III) ions occurs in two stages, and these results are consistent with other studies (for example, Gundogan et al., 2004; Zhao et al., 2011). In the first stage (in the first five minutes) a very rapid adsorption was observed – 95 % and 86 % of copper (II) and chromium (III) ions were adsorbed, respectively. In the second stage, the sorption equilibrium was gradually reached. In the case of copper(II) ions equilibrium was reached in 10 minutes and 96 % of metal ions were adsorbed. The equilibrium towards chromium(III) ions was reached in 30 minutes and 95 % of metal ions were adsorbed. Literature offers two explanations for this sorption character. The first rapid stage of the sorption can be explained by the fact that the ions are adsorbed on the outer surface of the sorbent, while in the second stage, the diffusion of metal ions takes place in the volume of the sorbent, therefore sorption takes place more slowly (Aringhieri, 1985). According to Ting (1989), in the first stage the physical sorption (or ion exchange) is taking place on the peat particle surface, while the sorption takes place more slowly at the second phase, as the saturation of sorption sites are gradually increasing. Results from kinetic studies were analyzed using the pseudo-first order and pseudo-second order equations (Lagergren, 1898; Ho and McKay, 1998; Ho and McKay, 2004). Based on the coefficients of determination (r^2), the sorption of both copper(II) and

chromium(III) ions by bog peat is best described by the pseudo-second order equation, as in both cases $r^2 = 1$. The pseudo-first order equation can be used to describe the kinetic data of chromium(III) sorption, as $r^2 = 0.71$. However, the kinetic data from the study where peat was used for the removal of copper(II) ions, cannot be described by the pseudo-first order equation, as $r^2 = 0.02$. Other studies also show that the pseudo-second order equation has a better correlation with the experimentally obtained data compared to the pseudo-first order equation (for example, Gundogan et al., 2004; Cochrane et al., 2006; Balan et al., 2009a).

The effect of pH

The effect pH has on peats ability to adsorb chromium(III) and copper(II) ions was evaluated at 20 °C using Kaigu 125–145 cm and the peat solution with the metal concentration of 25 mg/L. The results showed that the sorption character is very similar for the both studied metals – the lowest sorption capacity was observed at pH 2.0, where 17.6 % and 30.4 % of chromium (III) and copper (II) ions were adsorbed, respectively. The maximum sorption capacity was observed at pH 9 – the removal of chromium(III) and copper(II) ions reached 97.8 % (sorption capacity – 1.96 mg/g) and 97.2 % (1.94 mg/g), respectively. The observed sorption character (the increase of the sorption capacity with the increase of the pH value) is relatively widely described in the literature (for example, Ma and Tobin, 2004; Qin et al., 2006) – this is due to the increasing competition between the H^+ ions and metal cations for the adsorption sites in the system (Fiol et al., 2003; Abdel-Ghani et al., 2007).

3.3. Removal of phosphates by peat modified with iron hydroxide

3.3.1. Characteristics of the sorbents

Peat sample is characterized by high concentration of organic matter and average degree of decomposition (Table 3.3.1.). Slightly decomposed peat was used, as it exhibits better hydraulic properties (Couillard, 1994). If a sorbent is to be used on an industrial scale, besides having a high sorption capacity, it should be cheap and easily available in large quantities. Therefore, the peat used in this study was obtained from a commercially harvested raised bog.

It was confirmed that the modification has improved one of the most important properties of a sorbent – specific surface area. The specific surface area of the modified peat compared to the unmodified peat increased by 14.5 times. It is indicated that the increase of specific surface area of the sorbent, increases the sorption capacity of phosphate ions (Onar et al., 1996; Lyngsie et al., 2014).

The Fourier transform infrared spectroscopy confirmed the interaction of iron(III) hydroxy ions with peat carboxylic groups (Figure 3.3.1.) The FTIR spectra exhibited the absorption bands typical for peat, whereas after the modification of peat, the carboxylic group bands (at 1720 cm^{-1}) disappeared, and the carboxylic ion (at 1580 and 1400 cm^{-1}) and hydroxyl group (at 3420 cm^{-1}) absorption increased, which clearly indicates complex formation between peat and iron compounds (Anson et al., 2013).

Table 3.3.1.

Characteristics of raw peat and modified peat

Peat type	Raw peat	Modified peat				
	<i>Sphagnum fuscum</i> peat					
pH (in H ₂ O)	3.31	5.15				
Organic matter, %	96.6	83.4				
Decomposition degree, %	22	-				
C, %	46.57	32.98				
H, %	5.52	4.48				
N, %	0.96	0.66				
S, %	< 0.5	0.0				
Specific surface area BET, m ² /g	3.02	43.80				
Zero point of charge	2.43	3.68				
Concentration of iron, mg/kg	789	125000				
Particle size distribution (before modification/ after modification), %						
<0.05 mm	0.05– 0.125 mm	0.125– 0.250 mm	0.25– 0.50 mm	0.5–1.0 mm	1.0–2.0 mm	> 2.0 mm
1.0/ 1.1 %	7.0/ 6.5 %	18.2/ 8.6 %	29.7/ 14.6 %	28.6/ 22.3 %	15.5/ 36.1 %	0.0/ 10.8 %

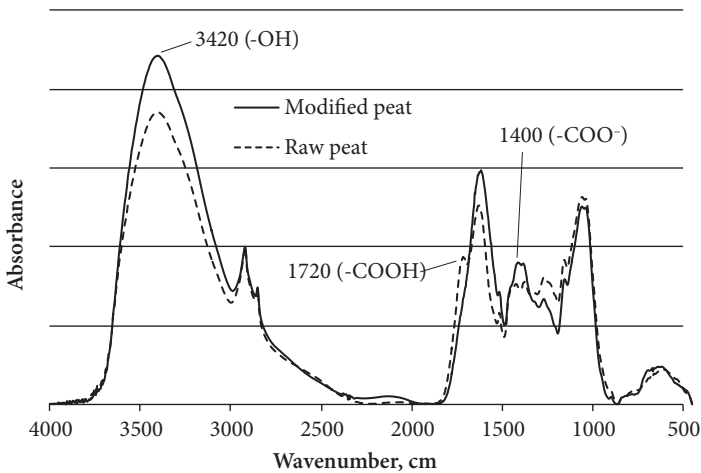


Figure 3.3.1. The FTIR spectra of peat and iron-modified peat

The composition of iron-modified peat was analyzed by XRD, which showed no obvious diffraction peaks (data not shown), indicating that the modified peat was X-ray amorphous.

3.3.2. Removal of phosphate from synthetic solutions

The determination of maximum sorption capacity and effect of temperature

As seen from Figure 3.3.2., the sorption capacity of modified peat increased with the increase of the initial phosphate concentration for all temperatures studied. The steep rise of the isotherm curves close to the origin indicates high uptake values at lower phosphate concentrations. At the initial phosphate concentrations of 0.1–25 mg P/L, 99 % of phosphate ions were removed. The maximum sorption capacity of modified peat reached 11.20 mg P/g at 20 °C and the initial phosphate concentration of 500 mg P/L. As the temperature of wastewater can change significantly depending on the season, it is important to know the effect of temperature on sorption performance. The maximum sorption capacity of peat increased from 9.64 mg P/g to 11.53 mg P/g when the temperature was changed from 2 °C to 40 °C. The increase in the sorption effectiveness caused by the increase in temperature indicates the endothermic nature of sorption (Mezenner and Bensmaili, 2009).

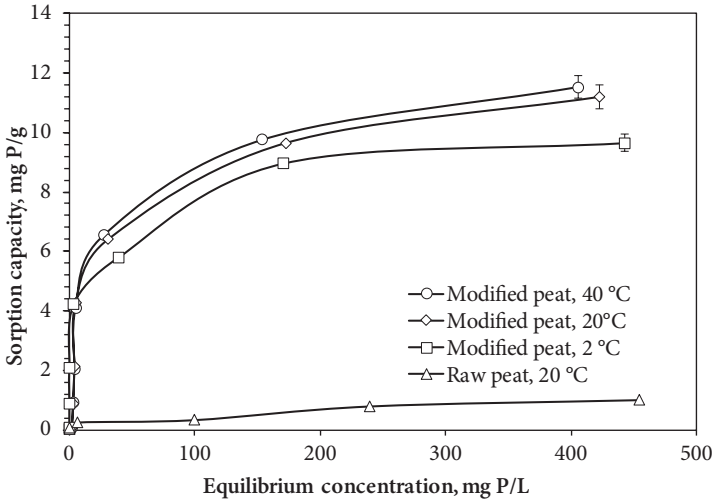


Figure 3.3.2. Effect of initial concentration and temperature on the removal of phosphate ions by raw and modified peat ($m = 1.0$ g; $V = 80$ mL; $t = 24$ h; relative standard deviation $\leq 3,6$ %)

The Langmuir equation was used to describe the experimental data of the isotherms:

$$q_e = \frac{b C_e q_{max}}{1 + b C_e} \quad (\text{Eq. 3.1.})$$

This equation uses two parameters – i.e., q_{max} (the maximum sorbate uptake under the given conditions) and b (the Langmuir constant) – which reflect the nature of the sorbent and is useful to compare the sorption performance quantitatively (Holan and

Volesky, 1994; Davis et al., 2000). The calculation of q_{\max} values is also useful in the situations when equilibrium is not reached in the sorption experiments (Volesky et al., 1993). It was proved that the Langmuir model very well describes the experimental data, as r^2 was > 0.99 at all temperatures applied in the study. The maximum sorption capacities estimated by the Langmuir model were 9.65, 11.12, and 11.62 mg P/g at 2, 20, and 40 °C respectively. The calculated Langmuir constant b indicated a greater affinity between the modified peat and phosphate ions at 40 °C than at 2 °C, as this constant decreased with increasing temperature (2 °C: $b = 0.177$; 20 °C: $b = 0.155$; 40 °C: $b = 0.090$). In general, a lower value of b indicates a higher affinity (Kratochvil and Volesky, 1998).

The sorption capacity of modified peat obtained in this study can be regarded as relatively high and could be compared to other materials reported in literature (Table 3.3.2.).

Table 3.3.2.

Comparison of the sorption capacity of iron-modified peat with the values presented in literature

Material	Sorption capacity, mg P/g	Reference
Raw (unmodified) peat	0.92	This study
Iron-modified peat	11.53	This study
Electric arc furnace steel slag	0.13–0.28	Barca et al., 2012
Basic oxygen furnace steel slag	1.14–2.49	Barca et al., 2012
Mineral apatite	~0.30	Bellier et al., 2006
Shale	0.5	Cyrus and Reddy, 2010
Ferric and alum water treatment residuals (FARs)	28.4	Wang et al., 2011
Activated FARs	53.2	Wang et al., 2011
Different kinds of sand	0.13–0.29	Xu et al., 2006
Furnace slag	8.89	Xu et al., 2006
Iron oxide tailings	~9.00	Zeng et al., 2004

However, materials with a high phosphate sorption capacity should be tested in long-term experiments in full-size systems, because many of the materials showing a very high phosphate removal potential in laboratory experiments do not show similar behavior in full-scale systems.

Effect of contact time

The effect of contact time at the initial phosphate concentration of 25 mg P/L and sorbent mass of 1.0 g or 0.2 g is presented in Figure 3.3.3.

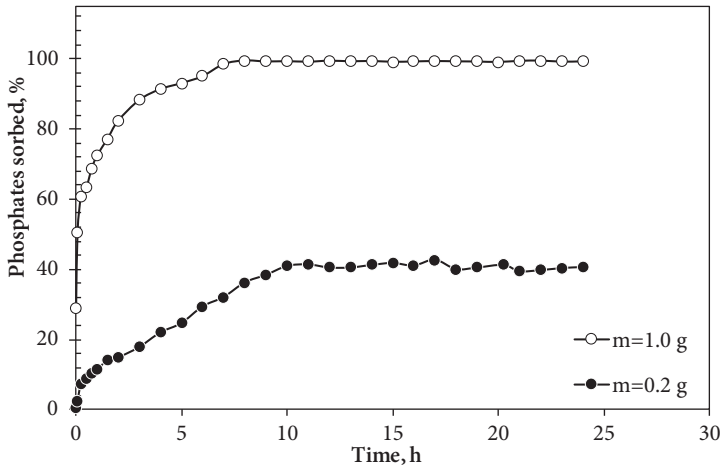


Figure 3.3.3. Effect of contact time on the uptake of phosphate ions by ($m = 1.0$ or 0.2 g; $V = 80$ mL; $C_i = 25$ mg P/L; $T = 20$ °C; $t = 1$ min – 24 h; relative standard deviation ≤ 4.0 %)

The results show that the removal of phosphate is very rapid with 1.0 g of sorbent used: 60.7 % of phosphates were sorbed in the first 15 minutes. In contrast, only 7.4 % of phosphates were sorbed with 0.2 g of sorbent used. In both cases, the first sorption stage was followed by a gradual increase in the amount of phosphate ions sorbed. The equilibrium was reached in 8 hours with 99.5 % phosphates sorbed ($m = 1.0$ g) or 10 hours with 40.9 % phosphates sorbed ($m = 0.2$ g). The data obtained from kinetic studies have been fitted to the pseudo-first order and pseudo-second order kinetic models. The results of the kinetic parameters for phosphate sorption are listed in Table 3.3.3.

Table 3.3.3.

Parameters for the kinetic models of phosphate sorption by modified peat

Mass of sorbent, g	q_e^* (mg/g)	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
		k_1 (L/min)	q_e (mg/g)	r^2	k_2 (g/(mg min))	q_e (mg/g)	r^2
0.2	4.11	0.012	4.79	0.83	0.001	4.72	0.88
1.0	2.10	0.016	0.96	0.88	0.037	2.02	0.99

* Actual (experimental) phosphate sorption capacity at equilibrium

Based on the coefficients of determination (r^2), the sorption of phosphates by modified peat is best described by the pseudo-second order equation. In addition, the equilibrium sorption capacities (q_e) calculated by the pseudo-second order model were closer to the experimental values.

Effect of pH

Environmental factors can influence the uptake of pollutants by different types of sorbents, and the pH of the solution sometimes is regarded as the most important one. Evaluation of the results of the first series (Figure 3.3.4.) can lead to the conclusion that pH has almost no effect. However, these results are caused by the high buffering capacity of peat. When the initial pH values were set to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0, the pH values after the sorption were 2.73, 5.61, 6.09, 6.23, 6.29, 6.42, 6.67, 6.74, and 6.81 respectively. In the second series, the pH was adjusted during the sorption (so that initial pH = final pH). Therefore, the results are more representative in this case. At the same time, the pH of the solution cannot be fully evaluated, as very high sorption effectiveness (99–100 % removal) was observed in the pH range 2–5. In order to evaluate the effect of pH accurately, the chosen sorbent/sorbate ratio and concentration of the initial solution must not lead to sorption effectiveness close to 100 % in any of the pH values. Therefore, a third series was conducted, and the results showed that the sorption capacity is strongly dependent on the pH of the solution. When the pH was set to 2.0, the sorption effectiveness reached 83.0 %, as compared to just 13.0 % at the pH 10.0. The different results obtained in each of the series point to the importance of the study methodology in these types of experiments.

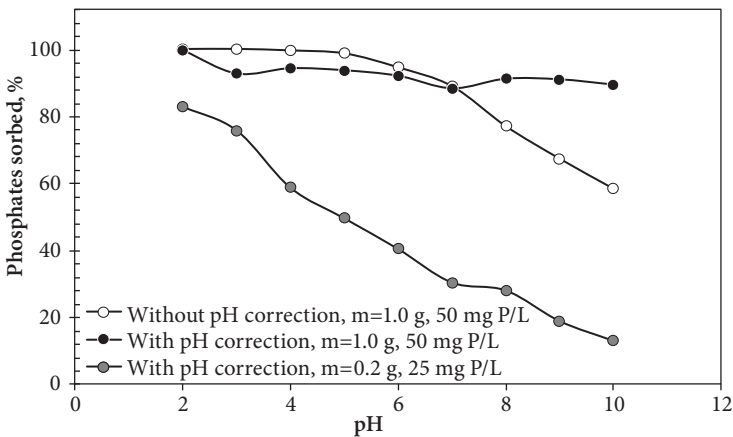


Figure 3.3.4. Effect of pH on the uptake of phosphate ions by modified peat
 ($m = 1.0$ g or 0.2 g; $V = 80$ mL; $C_i = 50$ or 25 mg P/L; $T = 20$ °C; $t = 24$ h;
 relative standard deviation ≤ 4.0 %)

Several explanations can be found in literature as to why the sorption capacity is higher at low pH values and decreases with the increase in pH. Lower sorption capacities are observed at high pH values, because there is competition for the sorption sites between phosphate species and OH^- ions (Boujelben et al., 2008). In addition, at high pH values, the iron oxides present in the material carry more negative charges, which repulse the negatively charged PO_4^{3-} species (Zeng et al., 2004).

Effect of ionic strength

Wastewater can contain all kinds of ions – such as SO_4^{2-} , Cl^- , CO_3^{2-} , NO_3^- , Mg^{2+} , Ca^{2+} , and Fe^{2+} – which can influence the sorption effectiveness of the selected material (Aryal and Liakopoulou-Kyriakides, 2011). The results show that sorption capacity was strongly affected when NaCl or Na_2SO_4 was added to the solution. Without the addition of NaCl or Na_2SO_4 , the sorption capacity reached 4.06 mg P/g (39.2 % removal). Compared to that, when the ionic strength was set to 0.05 mol/L by NaCl or Na_2SO_4 , the sorption capacity reached 5.90 mg P/g (59.0 % removal) and 5.19 mg P/g (51.9 % removal) respectively. However, the further increase in the ionic strength (from 0.05 to 1.0 mol/L) resulted in a small additional effect on the uptake of phosphate ions, as the removal capacity reached 53–55 % in the case of Na_2SO_4 and 63–67 % in the case of NaCl. The presence of the divalent anion SO_4^{2-} has a lower effect on the phosphate sorption than the monovalent Cl^- anion, which might indicate that the charge density of the chosen anion plays a significant role. Su and coworkers (2013) also have found a higher sorption capacity of zirconium oxide nanoparticles towards phosphates with the increase of the ionic strength. This effect was justified by the findings of McBride (1997), who linked the increase in sorption efficiency with the formation of inner-sphere complexes. In the case of formation of outer-sphere complexes, the decrease in sorption efficiency with the increase in ionic strength would be observed. In addition, according to Ryden and Syers (1975), the increase of ionic strength increases the removal of phosphate ions, as higher ionic strength reduces the thickness of the diffusion layer.

3.3.3. Removal of phosphate from wastewater

The sorption capacity of the sorbent could be significantly lower if a real wastewater is used instead of the synthetic solutions, as phosphate ions may compete for the sorption sites with other ions present in the wastewater. Taking into account this possibility, wastewater samples from two different sources were used to evaluate the sorption performance of the iron modified peat. The “Wastewater A” was obtained from a septic tank serving a household of 2 persons. The “Wastewater B” was taken from a wastewater treatment plant. The plant has a maximum design capacity of 350000 m^3 per day. Characteristics of the “Wastewater A” were as follows: biochemical oxygen demand = 160 mg/L; chemical oxygen demand = 464 mg/L; total nitrogen = 168 mg/L; total phosphorus = 23 mg/L; phosphates = 12.4 mg/L; total suspended solids = 83 mg/L; and pH = 7.70. Characteristics of the “Wastewater B” were as follows: biochemical oxygen demand = 290 mg/L; chemical oxygen demand = 583 mg/L; total nitrogen = 52.2 mg/L; total phosphorus = 6.67 mg/L; phosphates = 3.62 mg/L; total suspended solids = 449 mg/L; and pH = 7.60. Batch tests indicated that iron-modified peat can remove phosphates from wastewater with a very high efficiency: 98.5 % of all phosphate ions were removed from the “Wastewater A”, meaning that the phosphate concentration in the wastewater was reduced from 12.40 to 0.22 mg P/l. The removal efficiency from the “Wastewater B” reached 98.2 %. Based on the sequential batch studies, it was determined that the maximum sorption capacity of iron-modified peat is 13.75 mg P/g, which is even higher than the value determined by isotherm studies using synthetic solutions (11.20 mg P/g).

3.3.4. Recycling of spent sorbent

Concentration of heavy metals in the spent sorbent

When the saturation capacity of the sorbent has been reached, appropriate utilization of the spent sorbent is necessary. If the sorbent is utilized in land application, the concentration of heavy metals should be within safe limits. The modified peat was saturated with phosphates from wastewater obtained from a septic tank serving a household of 2 persons. Accordingly, the concentrations of heavy metals in the spent sorbent were compared to the limit values for wastewater sludge established by some countries in the European Union (Table 3.3.4.).

Table 3.3.4.

Concentration of metals in raw, modified peat and spent sorbent compared with some limits for heavy metal concentrations in sludge for application to soil (European Commission, 2001)

		Ni	Cu	Zn	Cd	Pb
Concentration of heavy metals, mg/kg	Raw peat	<0.50	0.51	2.49	<0.10	7.91
	Iron-modified peat	234.54	70.80	10.68	<0.10	17.62
	Spent sorbent	160.91	72.83	80.01	<0.10	13.99
Limit values, mg/kg	France	200	1000	3000	20	800
	Germany	200	800	2500	10	900
	Spain, – soil pH < 7	300	1000	2500	20	750
	Spain, – soil pH > 7	400	1750	4000	40	1200
	Poland	100	800	2500	10	500
	Latvia	300	1000	2500	20	750

The results showed that modification significantly increased the concentration of heavy metals in peat when the purified grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used. However, the concentrations of these elements in the spent sorbent were below the limit values; therefore, the phosphate-saturated peat could be suitable for dispersion into soil in a similar manner as wastewater sludge is used in agriculture. Moreover, the concentration of heavy metals in the modified peat could be significantly reduced by using a higher grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, although this would increase the total costs of the developed sorbent.

Phytotoxicity test

In order to test the phytotoxicity of the spent sorbent, the cress seed germination test (with garden cress (*Lepidium sativum*)) was used (Zucconi et al., 1981). This test integrates all the potentially harmful effects (for example – increased concentration of heavy metals) and is a sensitive parameter for a rapid evaluation of phytotoxicity. The calculated germination indexes for raw peat and modified peat were 31.2 and 24.3 %, respectively. The results showed that a fresh sorbent significantly inhibited the seed germination and growth (unlike the spent sorbent), probably due to the salts precipitated on the surface of the sorbent during the modification – the concentration of Na ions in the sorbent reached 76.3 mg/g. The calculated germination index value for spent sorbent

(69 %) was higher than 50 %, which indicates that the spent sorbent is non-toxic for plants (Zucconi et al., 1981) and can potentially be used as an organic soil amendment. This type of utilization provides an additional benefit for the use of iron-modified peat, as it has been indicated that, in the case of traditional methods (e.g., chemical precipitation), it is very difficult or even impossible to recycle phosphorus in an economical industrial manner (De-Bashan and Bashan, 2004). In general, peat can be used to improve the quality of soil, as it increases the water-holding capacity and content of organic carbon.

CONCLUSIONS

1. The aim of the research of biosorption is to find a more environmentally friendly alternative to traditional treatment methods, which in many cases cannot be used or is not economically feasible. Peat is one of the most widely studied biosorbent, and its benefits are determined by its unique physicochemical properties, as well as the fact that peat is a relatively cheap and widely available material which is easy to handle.
2. There are different understandings among researchers as far as what is biosorption, what are the mechanisms determining biosorption, and a unified definition of the term biosorption has not been developed, therefore making it necessary to clearly define mechanisms involved in the biosorption and their role in the process of biosorption.
3. Peat is an effective biosorbent to bind chromium(III) and copper(II) ions in aqueous solutions. The adsorbed amount of copper(II) and chromium(III) ions depends on the concentrations of the initial solution, pH of the solution, and contact time between the solution and peat. Kinetic studies showed that the sorption takes place very rapidly and sorption kinetic data are best described by the pseudo-second order equation.
4. For the first time it has been demonstrated that it is possible to use peat for the sorption of monovalent heavy metal ions, i.e., thallium(I) ions. Sorption process is exothermic, equilibrium occurs relatively quickly (within 25 minutes, when the concentration of the initial solution is 10 mg/L), and the sorption capacity of peat is significantly reduced with presence of the interfering ions in the solution.
5. By modifying bog peat with iron hydroxide, a new sorbent has been developed, which can be used to treat water polluted with phosphate ions. The suitability of its use has been determined by several factors – by use of a relatively simple modification method a new material with high sorption capacity has been developed; a high sorption capacity has been observed not only by using synthesized wastewater, but also by wastewater samples; the sorption of phosphate ions occurs relatively fast.
6. Taking into account that the peat saturated with phosphate ions does not show phytotoxicity and the concentration of heavy metals in the material is lower than the limit values, it is reasonable to believe that phosphate saturated peat (e.g., spent sorbent) can be utilized by land application.

REFERENCES

1. Abdel-Ghani, N.T., Hefny, M., El-Chaghaby, G.A.F. (2007) Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science and Technology*, 4, 67-73.
2. Aringhieri, R., Carrai, P., Petruzzelli, G. (1985) Kinetics of Cu^{2+} and Cd^{2+} adsorption by an Italian soil. *Soil Science*, 139(3), 197-204.
3. Ansone-Bērtiņa, L. (2015) *V un VI grupas metaloīdu sorbcijas izpēte uz modificētiem biomateriālu sorbentiem*. Rīga: LU Akadēmiskais apgāds, 119.
4. Aryal, M., Liakopoulou-Kyriakides, M. (2011) Equilibrium, kinetics and thermodynamic studies on phosphate biosorption from aqueous solutions by Fe(III)-treated *Staphylococcus xylosum* biomass: common ion effect. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 387(1-3), 43-49.
5. Asapo, E.S. (2011) *An adsorption study of nickel and cobalt on saprist Newfoundland peat*. St. John's: Memorial University of Newfoundland, 242.
6. Balan, C., Bilba, D., Macoveanu, M. (2009) Studies on chromium(III) removal from aqueous solutions by sorption on *Sphagnum* moss peat. *Journal of the Serbian Chemical Society*, 74, 953-964.
7. Barca, C., Gérente, C., Meyer, D., Chazarenc, F., Andrès, Y. (2012) Phosphate removal from synthetic and real wastewater using steel slags produced in Europe. *Water Research*, 46, 2376-2384.
8. Batista, A.P.S., Roméo, L.P.C., Arguelho, M.L.P.M., Garcia, C.A.B., Alves, J.P.H., Passos, E.A., Rosa, A.H. (2009) Biosorption of Cr(III) using in natura and chemically treated tropical peats. *Journal of Hazardous Materials*, 163, 517-523.
9. Bellier, N., Chazarenc, F., Comeau, Y. (2006) Phosphorus removal from wastewater by mineral apatite. *Water Research*, 40, 2965-2971.
10. Boujelben, N., Bouzid, J., Elouear, Z., Feki, M., Jamoussi, F., Montiel, A. (2008) Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents. *Journal of Hazardous Materials*, 151, 103-110.
11. Brown, P.A., Gill, S.A., Allen, S.J. (2000) Metal removal from wastewater using peat. *Water Research*, 34(16), 3907-3916.
12. Cerqueira, S.C.A., Romão, L.P.C., Lucas, S.C.O., Fraga, L.E., Simões, M.L., Hammer, P., Lead, J.R., Mangoni, A.P., Mangrich, A.S. (2012) Spectroscopic characterization of the reduction and removal of chromium(VI) by tropical peat and humin. *Fuel*, 91(1), 141-146.
13. Chong, K.H., Volesky, B. (1995) Description of two-metal biosorption equilibrium by Langmuir-type models. *Biotechnology and Bioengineering*, 47, 451-460.
14. Cochrane, E.L., Lu, S., Gibb, S.W., Villaescusa, I. (2006) A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *Journal of Hazardous Materials*, 137(1), 198-206.
15. Cojocar, C., Diaconu, M., Cretescu, I., Savić, J., Vasić, V. (2009) Biosorption of copper(II) ions from aqua solutions using dried yeast biomass. *Colloid Surface A*, 335, 181-188.
16. Couillard, D. (1994) The use of peat in wastewater treatment. *Water Research*, 28(6), 1261-1274.
17. Cyrus, J.S., Reddy, G.B. (2010) Sorption and desorption of phosphorus by shale: batch and column studies. *Water Science and Technology*, 61, 599-606.

18. Davis, T.A., Volesky, B., Vieira, R.H.S.F. (2000) *Sargassum* seaweed as biosorbent for heavy metals. *Water Research*, 34, 4270-4278.
19. Dean, S.A., Tobin, J.M. (1999) Uptake of chromium cations and anions by milled peat. *Resources, Conservation and Recycling*, 27, 151-156.
20. De-Bashan, L.E., Bashan, Y. (2004) Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*, 38, 4222-4246.
21. Fiol, N., Villaescusa, I., Martinez, M., Miralles, N., Poch, J., Serarols, J. (2003) Biosorption of Cr(VI) using low cost sorbents. *Environmental Chemistry Letters*, 1, 135-139.
22. Frostman, T.M. (1993) A peat/wetland treatment approach to acidic mine drainage abatement. In: G.A. Moshiri, *Constructed Wetlands for Water Quality Improvement* (pp. 197-200). Boca Raton, FL, CRC Press.
23. Gadd, G.M. (2009) Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *Journal of Chemical Technology and Biotechnology*, 84, 13-28.
24. Gardea-Torresdey, J.L., Tang, L., Salvador, J.M. (1996) Copper adsorption by esterified and unesterified fractions of *Sphagnum* peat moss and its different humic substances. *Journal of Hazardous Materials*, 48, 191-206.
25. Gündoğan, R., Acemioglu, B., Alma, M.H. (2004) Copper(II) adsorption from aqueous solution by herbaceous peat. *Journal of Colloid and Interface Science*, 269, 303-309.
26. Gupta, V.K., Carrott, P.J.M., Ribeiro-Carrot, M.M.L. (2009) Low-cost adsorbents: growing approach to wastewater treatment – a review. *Critical Reviews in Environmental Science and Technology*, 39, 783-842.
27. Harvey O.R., Rhue, R.D. (2008) Kinetics and energetics of phosphate sorption in a multi-component Al(III)-Fe(III) hydr(oxide) sorbent system. *Journal of Colloid and Interface Science*, 322, 384-393.
28. Heiri, O., Lotter, A.F., Lemcke, G. (2001) Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, 25, 101-110.
29. Ho, Y.S., Wase, D.A.J., Forster, C.F. (1995) Batch nickel removal from aqueous solution by *Sphagnum* peat moss. *Water Research*, 29, 1327-1332.
30. Ho, Y.S., McKay, G. (1998) Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal*, 70, 115-124.
31. Ho, Y.S., McKay, G. (2000) The kinetics of sorption of divalent metal ions onto *Sphagnum* moss peat. *Water Research*, 34(3), 735-742.
32. Ho, Y.S., McKay, G. (2003) Sorption of dyes and copper ions onto biosorbents. *Process Biochemistry*, 38(7), 1047-1061.
33. Ho, Y.S., McKay, G. (2004) Sorption of copper (II) from aqueous solution by peat. *Water, Air, and Soil Pollution*, 158, 77-97.
34. Holan, Z.R., Volesky, B. (1994) Biosorption of lead and nickel by biomass of marine algae. *Biotechnology and Bioengineering*, 43, 1001-1009.
35. Jacobson, A.R., McBride, M.B., Baveye, P., Steenhuis, T.S. (2005) Environmental factors determining the trace-level sorption of silver and thallium to soils. *Environment*, 345, 191-205.
36. Joosten, H., Clarke, D. (2002) *Wise Use of Mires and Peatlands*. Saarijärvi: International Mire Conservation Group and International Peat Society, 303.
37. Kalmykova, Y., Strömvall, A.M., Steenari, B.M. (2008) Adsorption of Cd, Cu, Ni, Pb and Zn on *Sphagnum* peat from solutions with low metal concentrations. *Journal of Hazardous Materials*, 152(2), 885-891.

38. Kratochvil, D., Volesky, B. (1998) Advances in the biosorption of heavy metals. *Trends in Biotechnology*, 16, 291-300.
39. Kyzioł, J., Twardowska, I., Schmitt-Kopplin, P. (2006) The role of humic substances in chromium sorption onto natural organic matter (peat). *Chemosphere*, 63, 1974-1982.
40. Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24(4), 1-39.
41. Lyngsie, G., Borggaard, O.K., Hansen, H.C.B. (2014) A three-step test of phosphate sorption efficiency of potential agricultural drainage filter materials. *Water Research*, 51, 256-265.
42. Ma, W., Tobin, J.M. (2004) Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium. *Biochemical Engineering Journal*, 18(1), 33-40.
43. Mayes, W.M., Batty, L.C., Younger, P.L., Jarvis, A.P., Kõiv, M., Vohla, C., Mander, U. (2009) Wetland treatment at extremes of pH: a review. *Science of the Total Environment*, 407, 3944-3957.
44. McBride, M.B. (1997) A critique of diffuse double layer models applied to colloid and surface chemistry. *Clays and Clay Minerals*, 45, 598-608.
45. McKay, G., Porter, J.F. (1997) Equilibrium parameters for the sorption of copper, cadmium and zinc ions onto peat. *Journal of Chemical Technology and Biotechnology*, 69, 309-320.
46. Memon, S.Q., Memon, N., Solangi, A.R., Memon, R. (2008) Sawdust: a green and economical sorbent for thallium removal. *Chemical Engineering Journal*, 140, 235-240.
47. Mezenner, N.Y., Bensmaili, A. (2009) Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chemical Engineering Journal*, 147, 87-96.
48. Murphy, J., Riley, J. (1962) A modified single solution for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27, 31-36.
49. Mohan, D., Pittman, J.C.U. (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of Hazardous Materials*, 137, 762-811.
50. Onar, N.A., Nilgum, B., Tanil, A. (1996) Phosphate removal by adsorption. *Environmental Technology*, 17, 207-213.
51. Onianwa, P.C. (2001) Monitoring atmospheric metal pollution: a review of the use of mosses as indicators. *Environmental Monitoring and Assessment*, 71, 13-50.
52. Pertusatti, J., Prado, A.G.S. (2007) Buffer capacity of humic acid: thermodynamic approach. *Journal of Colloid and Interface Science*, 314(2), 484-489.
53. Qin, F., Wen, B., Shan, X.Q., Xie, Y.N., Liu, T., Zhang, S.Z., Khan, S.U. (2006) Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat. *Environmental Pollution*, 144, 669-680.
54. Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W., Zhang, Q. (2009) Critical review in adsorption kinetic models. *Journal of Zhejiang University Science A*, 10(5), 716-724.
55. Rasmussen, G., Fremmersvik, G., Olsen, R.A. (2002) Treatment of creosote-contaminated groundwater in a peat/sand permeable barrier – a column study. *Journal of Hazardous Materials*, 93(3), 285-306.
56. Rentz, J.A., Turner, I.P., Ullman, J.L. (2009) Removal of phosphorus from solution using biogenic iron oxides. *Water Research*, 43, 2029-2035.
57. Ringqvist, L., Öborn, I. (2002) Copper and zinc adsorption onto poorly humified *Sphagnum* and *Carex* peat. *Water Research*, 36, 2233-2242.
58. Ringqvist, L., Holmgren, A., Öborn, I. (2002) Poorly humified peat as an adsorbent for metals in wastewater. *Water Research*, 36, 2394-2404.
59. Ryden, J.C., Syers, J.K. (1975) Rationalization of ionic strength and cation effects on phosphate sorption by soils. *Journal of Soil Science*, 24(4), 395-406.

60. Sangvanich, T., Sukwarotwat, V., Wiacek, R.J., Grudzien, R.M., Fryxell, G.E., Addleman, R.S., Timchalk, C., Yantasee, W. (2010) Selective capture of cesium and thallium from natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica. *Journal of Hazardous Materials*, 182(1-3), 225-231.
61. Sen-Gupta, B., Curran, M., Hasan, S., Ghosh, T.K. (2009) Adsorption characteristics of Cu and Ni on Irish peat moss. *Journal of Environmental Management*, 90(2), 954-960.
62. Silamiķele, I. (2010) *Humifikācijas un ķīmisko elementu akumulācijas raksturs augsto purvu kūdrā atkarībā no tās sastāva un veidošanās*. Rīga: LU Akadēmiskais apgāds, 172.
63. Song, X., Pan, Y., Wu, Q., Cheng, Z., Ma, W. (2011) Phosphate removal from aqueous solutions by adsorption using ferric sludge. *Desalination*, 280 384-390.
64. Su, Y., Cui, H., Li, Q., Gao, S., Shang, J.K. (2013) Strong adsorption of phosphate by amorphous zirconium oxide nanoparticles. *Water Research*, 47, 5018-5026.
65. Sun, Q.Y., Lu, P., Yang, L.Z. (2004) The adsorption of lead and copper from aqueous solution on modified peat-resin particles. *Environmental Geochemistry and Health*, 26(2-3), 311-317.
66. Svensson, B.M. Mathiasson, L., Mårtensson, L., Kängsepp, P. (2011) Evaluation of filter material for treatment of different types of wastewater. *Journal of Environmental Protection*, 2, 888-894.
67. Ting, Y.P., Lawson, F., Prince, I.G. (1989) Uptake of cadmium and zinc by the alga *Chlorella vulgaris*: II. Multi-ion situation. *Biotechnology and Bioengineering*, 37(5), 445-455.
68. Twardowska, I., Kyzioł, J., Goldrath, T., Avnimelech, Y. (1999) Adsorption of zinc onto peat from peatlands of Poland and Israel. *Journal of Geochemical Exploration*, 66(1-2), 387-405.
69. Vohla, C., Kõiv, M., Bavor, H.J., Chazarenc, F., Mander, Ü. (2011) Filter materials for phosphorus removal from wastewater in treatment wetlands – a review. *Ecological Engineering*, 37(1), 70-89.
70. Volesky, B., May, H. Holan, Z.R. (1993) Cadmium biosorption by *Saccharomyces cerevisiae*. *Biotechnology and Bioengineering*, 41, 826-829.
71. Volesky, B., Naja, G. (2005) Biosorption: application strategies. In: S.T.L. Harrison, D.E. Rawlings, J. Petersen (Eds.), *The 16th International Biotechnology Symposium: Book of proceedings* (pp. 531-542). Cape Town, South Africa: IBS – Compress Co.
72. Wang, J., Chen, C. (2009) Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27, 195-226.
73. Wang, C.H., Gao, S.J., Wang, T.X., Tian, B.H., Pei, Y.S. (2011) Effectiveness of sequential thermal and acid activation on phosphorus removal by ferric and alum water treatment residuals. *Chemical Engineering Journal*, 172, 885-891.
74. Xiong, J.B., Mahmood, Q. (2010) Adsorptive removal of phosphate from aqueous media by peat. *Desalination*, 259(1-3), 59-64.
75. Xu, D., Xu, J., Wu, J., Muhammad, A. (2006) Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere*, 63, 344-352.
76. Zhao, G., Wu, X., Tan, X., Wang, X. (2011) Sorption of heavy metal ions from aqueous solutions: a review. *The Open Colloid Science Journal*, 4, 19-31.
77. Zeng, L., Li, X., Liu, J. (2004) Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research*, 38, 1318-1326.
78. Zucconi, F., Forte, M., Monac, A., De Bertoldi, M. (1981) Biological evaluation of compost maturity. *Biocycle*, 22, 27-29.