



A novel peat-based biosorbent for the removal of phosphate from synthetic and real wastewater and possible utilization of spent sorbent in land application

Artis Robalds^{a,*}, Liga Dreijalte^a, Oskars Bikovens^b, Maris Klavins^a

^aDepartment of Environmental Science, University of Latvia, Raina Blvd. 19, Riga LV-1586, Latvia, Tel. +371 26769597; email: artis.robalds@lu.lv (A. Robalds), Tel. +371 28380100; email: liga.dreijalte@gmail.com (L. Dreijalte), Tel. +371 29479430; email: maris.klavins@lu.lv (M. Klavins)

^bLaboratory of Lignin Chemistry, Latvian State Institute of Wood Chemistry, Dzerbenes Street 27, Riga LV-1006, Latvia, Tel. +371 29513922; email: bikovens@edi.lv

Received 7 August 2014; Accepted 20 May 2015

ABSTRACT

Removal of potentially harmful phosphorus compounds from wastewater by adsorption onto biosorbents is a cost-effective alternative to the conventional treatment methods. Raw peat and peat modified with iron(III) hydroxy ions were used in this study to remove phosphate ions from synthetic solution and household wastewater. Interaction of iron(III) ions with carboxylic groups of peat occurred during peat modification, which was confirmed by the FTIR technique. The effect of the initial phosphate concentration, pH, contact time, temperature, and ionic strength was studied in batch experiments. It was found that the sorption capacity increased with the increasing temperature, i.e. the maximum sorption capacity of the modified peat was 9.64 mg P/g at 2°C and 11.53 mg P/g at 40°C, respectively, indicating the endothermic nature of the sorption. Besides, the Langmuir equation was used to describe the sorption isotherms quantitatively. Given that the spent biosorbent did not exhibit phytotoxicity and the concentration of heavy metals did not exceed the limit values, the phosphate-saturated modified peat may be utilized as an organic fertilizer in agricultural land application.

Keywords: Adsorbent; Biosorption; Peat; Phosphate; Recovery; Removal; Sorption; Wastewater

1. Introduction

Excessive amounts of phosphorus compounds in surface waters can lead to eutrophication, which is a serious environmental problem in many countries around the world. Eutrophication causes depletion of oxygen, blooms of toxic algae, and degradation of water quality [1,2].

Discharge of raw or treated domestic wastewater is one of the main causes of eutrophication [3]. Therefore, effective wastewater treatment methods, which ensure efficient removal of phosphorus, must be used. When traditional wastewater treatment methods—such as biological treatment or chemical precipitation—cannot be used because of the high costs, low removal efficiency, large amounts of chemicals used or sludge produced, the use of sorbents is an alternative option [4]. Sorbents in this case are materials/filter media

*Corresponding author.

used in wastewater treatment and characterized by a high affinity for phosphorus [5]. One of the options is to use these materials/sorbents in constructed wetlands, which have been widely used for many years as a low-cost and low-maintenance alternative to treat phosphate-rich wastewater. However, the possibilities of removing phosphorus compounds in constructed wetlands are limited [5]. Therefore, we need specific media (sorbents) with a high phosphate sorption capacity and low cost. Taking into account that the known extractable sources of phosphate rock may be depleted in less than 100 years [6], there is a pressing need to recycle phosphorus contained in wastewater.

Peat is a prospective material for the removal of phosphate ions from aqueous solutions [7]. Although the sorption capacity of raw peat is low, we presume that it can be significantly increased by modifying peat with iron compounds. Naturally occurring iron-rich materials and waste products, such as low-grade iron ore [8], steel slags [9], red mud [10], ferric sludge [2], ferric water treatment residuals [11], iron oxides [12], iron-rich humus soils [13], iron oxide tailings [1], iron-rich calcareous soils [14], and goethite [15], are known for high affinities for phosphate sorption, and most of them have been tested as adsorbents in laboratory-scale experiments to remove phosphorus compounds.

Peat is a light brown to black organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, and trees [16]. 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 [17,18]. Consequently, the use of peat as a potential substrate in constructed wetlands has significant advantages compared to other biosorbents. Moreover, phosphate-saturated peat (i.e. spent sorbent) can be used to maintain soil structure, be a source of phosphorus in the soil, increase the content of organic matter, and improve moisture retention. So, peat can be used as a soil conditioner.

The aims of the study were to make a modified peat sorbent, to apply it in removing phosphates, and to evaluate the potential disposal of the spent sorbent as a soil conditioner.

2. Materials and methods

2.1. Preparation, characterization, and modification of the sorbent

All chemicals were of analytical grade (except $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, which was of purified grade) and they

were used without further purification. *Sphagnum fuscum* peat was collected from an industrially mined raised bog in Latvia. The peat sample was homogenized and sieved through a 2-mm sieve to remove large particles and then dried at 105°C for 24 h. The modified peat was prepared using an approach similar to that of Harvey and Rhue [19]: 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 12 h. The resulted precipitate was mixed well with 100 g of peat, filtered, washed with 250 ml deionized water, air-dried, and heated for 4 h at 60°C. The raw and modified peats were characterized by their botanical composition, major physical and chemical properties (through elemental analysis using a Carlo Erba EA 1108 Elemental Analyzer), pH (in H_2O ; 1:10 peat/water volume ratio), content of organic matter, and degree of decomposition (as shown in Table 1). The content of organic matter was measured after combusting a sample (1.0 g) at 550°C for 4 h and weighed. Total concentrations of metals in the peat, modified peat, and spent sorbent (i.e. modified peat after phosphate sorption) were analyzed using an atomic absorption spectrometer (PerkinElmer AAnalyst 200) after nitric acid digestion according to the EPA Method 3050B [20]. 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 Spectrum One apparatus (PerkinElmer). 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). The point of zero charge (pH_{ZPC}) was measured by the pH drift method.

2.2. Removal of phosphate from synthetic solution

The removal of phosphate ions from the aqueous synthetic solution was conducted using batch experiments, including: (1) isotherm studies at different temperatures, (2) kinetic studies, (3) pH studies, and (4) ionic strength studies.

Phosphate solutions were prepared by diluting the stock solution to the desired concentration using deionized water. The stock solution of phosphate (500 mg P/l) was prepared by dissolving 4.3936 g of KH_2PO_4 in 2,000 ml of deionized water.

If not stated otherwise, raw or modified peat (1.0 g) was mixed with 80 ml of the solution containing phosphate ions (25 mg P/l), then shaken on a rotary shaker with a constant speed of 140 rpm for

Table 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		125,000			
Particle size distribution (before modification/ after modification), % w/w ^a						
< 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%

^aSize fraction weight as a percentage of the total sample weight.

24 h at 20°C, and, finally, filtered before analysis of phosphate ions in the solution. No pH adjustments were made, except for the pH studies.

Isotherm studies were conducted at 2, 20, and 40°C using solutions with the concentrations of 1, 10, 25, 50, 100, 250, and 500 mg P/l. Kinetic studies were performed with sorption times in the range of 1 min–24 h, and sorbent mass $m = 1.0$ or 0.2 g. In order to determine the effect of ionic strength on phosphate sorption, appropriate amounts of NaCl or Na₂SO₄ were added to the phosphate solution in the range 0.05–1.00 mol/l. For the pH studies, the pH was adjusted in the range of 2–10 with 1.0, 0.5, or 0.1 M HCl, or NaOH using a pH meter (HANNA instruments pH 213). Different strategies were employed to study the effect of pH, namely, three series of tests were conducted: (1) without the pH adjustment during the sorption; initial concentration $C_i = 50$ mg P/l, $m = 1.0$ g; (2) pH was adjusted during the sorption (in 2, 4, and 22 h); $C_i = 50$ mg P/l, $m = 1.0$ g; and (3) pH was adjusted during the sorption (in 2, 4, and 22 h); $C_i = 25$ mg P/l, $m = 0.2$ g.

All sorption experiments were conducted in triplicate and the mean values were used. The relative standard deviation in all cases was less than 4.0%.

2.3. Test of kinetic models

The kinetic data were analyzed using two kinetic models: the Lagergren's first-order-rate equation [21], also called the pseudo-first-order model [22], and the pseudo-second-order model (Eqs. (1) and (2) as given below).

The most popular form of the pseudo-first-order model is the following:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (1)$$

and the pseudo-second-order model is generally expressed as [23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (2)$$

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium at any time, while k_1 (L/min) is the rate constant for the pseudo-first-order adsorption model and k_2 (g/mg min) is the rate constant for the pseudo-second-order model.

2.4. Removal of phosphate from wastewater

Modified peat (1.0 g) and wastewater (80 ml) were filled into glass bottles (100 ml), which were shaken at 140 rpm for 24 h. Then the wastewater was filtered, and the filtrate was analyzed for phosphates. Wastewater from two different sources was used in the experiments. The "Wastewater A" was obtained from a septic tank serving a household of three persons. The "Wastewater B" was taken from a wastewater treatment plant. The plant has a maximum design capacity of 350,000 m³ per day. The wastewater was characterized according to the Standard Methods for Examination of Water and Wastewater [24]. 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.

In order to determine the maximum sorption capacity and to obtain the material for phytotoxicity tests, 15 g of modified peat was mixed with 15 l of the “Wastewater A”. After 24 h, the suspension was filtered, and the filtrate was analyzed for phosphates. After filtration, the modified peat was collected, added to 15 l of untreated wastewater and mixed for 24 h once again. This procedure (i.e. sequential batch studies) was repeated five times until the full saturation capacity was reached (the phosphate concentration in the supernatant was the same as in the initial solution).

2.5. Phosphate analysis

The phosphate content in the filtrates, initial solutions, and wastewater was determined by the molybdenum blue spectrophotometric method at λ_{\max} of 880 nm [25] using a Hach Lange DR 2800 spectrophotometer.

2.6. Phosphate uptake

The sorption capacity (expressed by the mass of phosphorus sorbed/mass of sorbent) was calculated from the decrease in phosphate concentration in the solutions. To calculate the sorption capacity of phosphate onto peat (mg P/g), the following equation was used:

$$q_e = \frac{(C_i - C_e) \times V}{1000 \times m} \quad (3)$$

where q_e is the equilibrium sorption capacity (mg/g), V is the volume of phosphate solution (ml), m is the mass of peat used (g), and C_i and C_e are the initial and final (equilibrium) concentrations (mg/l).

2.7. Phytotoxicity test

The cress seed (*Lepidium sativum*) germination index (GI) was used to estimate the phytotoxicity of

raw peat, modified peat, and phosphate-saturated peat (i.e. spent sorbent). Peat or raw peat (10 g) was placed in Petri dishes, wetted with deionized water (30 ml), and covered with filter paper. Twenty *L. sativum* seeds were placed on the paper and kept in the dark for 48 h at 25°C. The GI was calculated by multiplying the germination and root elongation according to the formula:

$$GI = \left(\frac{G}{G_0}\right) \times \left(\frac{L}{L_0}\right) \times 100 \quad (4)$$

where G and L are the values of germinated seeds and root length in the spent sorbent, and G_0 and L_0 are values of these parameters in the control sample [26].

3. Results and discussion

3.1. Characteristics of raw peat and sorbent

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. Slightly decomposed peat was used, as it exhibits better hydraulic properties [27].

Raw peat was modified with iron(III) hydroxy ions using the sol-gel approach [28]. At the first stage of sorbent modification, we obtained colloidal suspension or sol of Fe(III) hydroxide. Its heating and reaction with the raw peat led to the formation of a gel-like structure.

The sorbent obtained can be considered as an organic-inorganic hybrid material, where the poly-functional iron compounds have modified the sorbent properties. The Fourier transform infrared spectroscopy confirmed the interaction of iron(III) hydroxy ions with peat carboxylic groups. The FTIR spectra exhibited the absorption bands typical for peat, whereas after the modification of peat, the carboxylic group bands disappeared, and the carboxylic ion and hydroxyl group absorption increased. The differential spectrum (Fig. 1, spectrum 3) shows a decrease in absorbance at 1,720 cm^{-1} (–COOH) and its increase at 3,420 cm^{-1} (–OH), 1,580 and 1,400 cm^{-1} (–COO–). The decreasing carbonyl group (at 1,720 cm^{-1}) and increasing carboxylic anion signal (at 1,580 and 1,400 cm^{-1}) clearly indicate complex formation between peat and iron compounds [29]. The interaction between Fe(III) and peat carboxylic group preserves the amorphous iron phase (that was confirmed by XRD), which could be important for phosphate sorption.

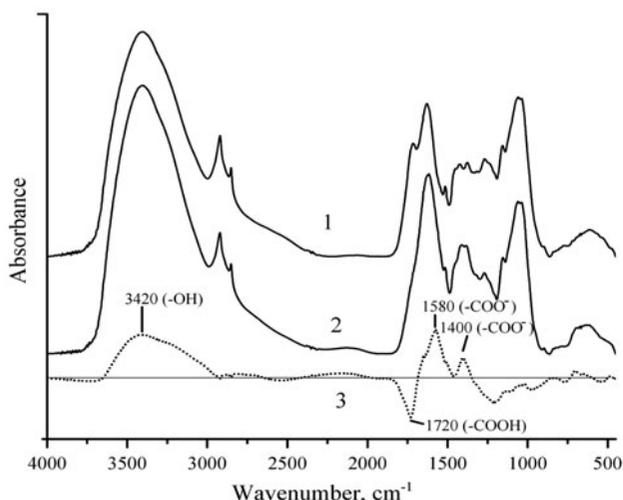


Fig. 1. The FTIR spectra of peat and iron-modified peat. (1) raw peat, (2) peat modified with ferric hydroxide, and (3) differential spectrum.

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.

The particle-size distribution in the modified peat shows that approximately 50% of all particles are larger than 1 mm. Michalak and coworkers [30] have reported the findings of Kuyucak [31], who had stated that the optimum sorbent particle size should be between 1 and 2 mm. To reduce possible clogging of the wastewater treatment system because of the small particle size, these particles could be granulated. Although it is necessary to obtain the desired granule properties, it should be pointed out that “granulation is more of a trial-and-error task making it difficult for academic researchers to make a significant contribution” [32].

3.2. Phosphate removal from synthetic solutions

3.2.1. Effect of initial phosphate concentration and temperature

To evaluate the removal of phosphate ions from aqueous solution by iron-modified peat at different temperatures, the sorption isotherms derived from the equilibrium batch sorption experiments were used. Primarily, the studies showed that raw peat had a sorption capacity below 1 mg P/g. As seen from Fig. 2, the sorption capacity of the modified peat increased with the increase in the initial phosphate concentration for all temperatures studied. The steep rise of the isotherm curves close to the origin indicates

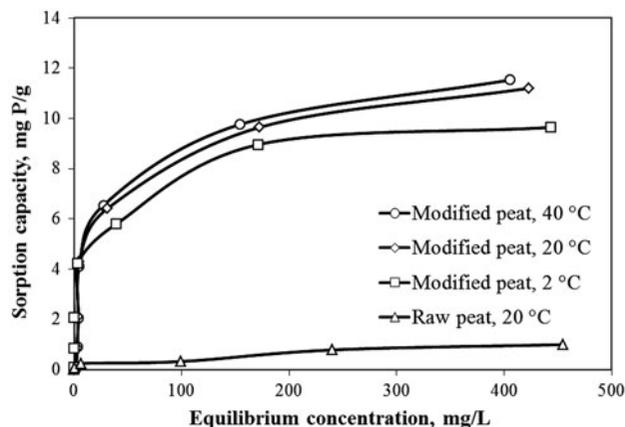


Fig. 2. Effect of the initial concentration and temperature on the removal of phosphate ions by raw and modified peat: 1.0 g of sorbent, 80 ml solution, 24 h contact time. Relative standard deviation was less than 3.6% in all cases.

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 the 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 to 11.53 mg P/g when the temperature was changed from 2 to 40 °C. The increase in the sorption effectiveness caused by the increase in temperature indicates the endothermic nature of sorption [33].

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

$$q_e = \frac{bC_e q_{\max}}{1 + bC_e} \quad (5)$$

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 are useful to compare the sorption performance quantitatively [34,35]. Besides, the calculation of q_{\max} values is useful in the situations when equilibrium is not reached in the sorption experiments [36].

It was proved that the Langmuir model very well describes the experimental data, as r^2 was > 0.99 at all temperatures applied in our 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 the 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 [37].

The sorption capacity of the modified peat obtained in this study can be regarded as relatively high and could be compared to other materials reported in the literature (Table 2). However, materials with a high P sorption capacity should be tested in long-term experiments in full-size systems, because many of the materials showing a very high phosphorus removal potential in laboratory experiments do not show similar behavior in full-scale systems.

3.2.2. Effect of contact time

Kinetic performance is among the most important factors in evaluating the suitability of the material to be used in full-scale systems [40]. Sorption kinetic experiments are performed to determine the point of equilibrium, i.e. point where sorption reaction is completed and there is no change in sorbate concentration in the solution.

The effect of contact time at the initial phosphate concentration of 25 mg P/l and sorbent mass of 1.0 or 0.2 g is presented in Fig. 3. 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 min. 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 h with 99.5% P sorbed ($m = 1.0$ g) or 10 h with 40.9% P 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

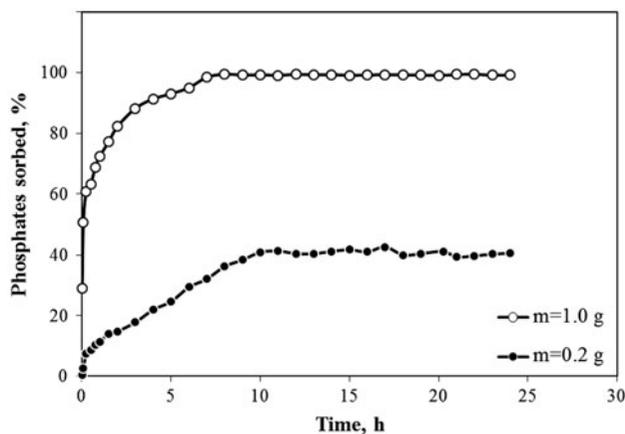


Fig. 3. Effect of contact time on the uptake of phosphate ions by the modified peat: 1.0 and 0.2 g of sorbent, 80 ml of 25 mg P/l, 1 min to 24 h contact time, 20°C. Relative standard deviation was less than 4.0% in all cases.

parameters for phosphate sorption are listed in Table 3. Based on the coefficients of determination (r^2), the sorption of phosphates by the 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.

3.2.3. 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 (Fig. 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

Table 2

Comparison of the sorption capacity of iron-modified peat with the values presented in the 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	[9]
Basic oxygen furnace steel slag	1.14–2.49	[9]
Different kinds of sand	0.13–0.29	[38]
Furnace slag	8.89	[38]
Mineral apatite	~0.3	[39]
Shale	0.5	[5]
Iron oxide tailings	~9.0	[1]

Table 3

Parameters for the kinetic models of phosphate sorption by the modified peat

Mass of sorbent, g	q_e^a (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

^aActual (experimental) phosphate sorption capacity at equilibrium.

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 a 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 the 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.

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 a competition for the sorption sites between phosphate species and OH^- ions [41]. 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 [1].

3.2.4. 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 [42]. The results show that sorption capacity was strongly affected when NaCl or Na_2SO_4 was added to the solution (Fig. 5). 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

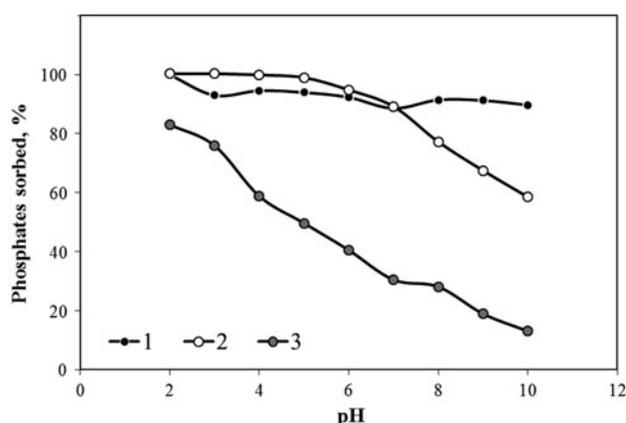


Fig. 4. Effect of pH on the uptake of phosphate ions by the modified peat: (1) without pH adjustment, 1.0 g of sorbent, 80 ml of 50 mg P/l, 24 h contact time, 20°C; (2) with pH adjustment, 1.0 g of sorbent, 80 ml of 50 mg P/l, 24 h contact time, 20°C; and (3) with pH adjustment, 0.2 g of sorbent, 80 ml of 25 mg P/l, 24 h contact time, 20°C. Relative standard deviation was less than 4.0% in all cases.

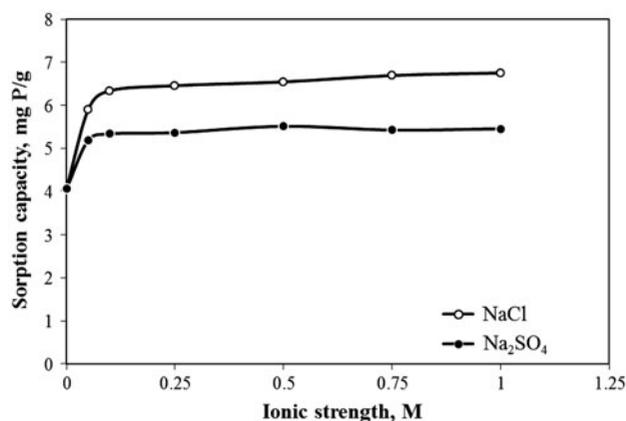


Fig. 5. Effect of ionic strength on the uptake of phosphate ions by the modified peat: 0.2 g of sorbent, 80 ml of 25 mg P/l, 24 h contact time, 20°C. Relative standard deviation was less than 2.2% in all cases.

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 [43] also have found a higher sorption capacity of zirconium oxide nanoparticles toward phosphates with the increase in the ionic strength. This effect was justified by the findings of McBride [44], 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 [45], the increase in ionic strength increases the removal of phosphate ions, as higher ionic strength reduces the thickness of the diffusion layer.

3.3. Phosphate removal from wastewater

The sorption capacity of the tested sorbent could be significantly lower if a real wastewater was 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 from two different sources was used to evaluate the sorption performance of the developed sorbent. 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%. It can be hypothesized that there is no significant effect of the wastewater composition on the removal of phosphates,

as a high removal efficiency was observed in both cases. 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).

3.4. Recycling of spent sorbent

3.4.1. 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. 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. 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 (Table 4). 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.

3.4.2. Phytotoxicity test

The cross seed germination test, which integrates all the potentially harmful effects of the substances present in the sample, is a sensitive parameter for rapid evaluation of phytotoxicity. The calculated germination

Table 4

Concentration of metals in raw and modified peat compared with some maximum acceptable limits for heavy metal concentrations in sewage sludge for application to soil [46]

		Ni	Cu	Zn	Cd	Pb
Concentration of heavy metals, mg/kg	Raw peat	<0.50	0.51	2.49	<0.10	7.91
	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	1,000	3,000	20	800
	Germany	200	800	2,500	10	900
	Spain, soil pH < 7	300	1,000	2,500	20	750
	Spain, soil pH > 7	400	1,750	4,000	40	1,200
	Poland	100	800	2,500	10	500
	Latvia	300	1,000	2,500	20	750

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 calculated GI value for spent sorbent (69%) was higher than 50%, which indicates that the spent sorbent is non-toxic for plants [26] 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 [3]. In general, peat can be used to improve the quality of soil, as it increases the water-holding capacity and content of organic carbon [47].

4. Conclusions

Peat is a material with unique characteristics, and it has significant advantages when compared with other biosorbents. The phosphate sorption capacity of peat was significantly increased by the modification with iron(III) hydroxy ions. It was proved that the developed sorbent can be used as a highly effective material to remove phosphate ions from aqueous media—both synthetic solutions and real wastewater. Considering the phytotoxicity tests and concentration of heavy metals in the spent sorbent, it was concluded that phosphate-saturated peat (spent sorbent) can be utilized in land application, which would eliminate the need of costly disposal of the material in landfills. However, additional experiments should be carried out to evaluate the suitability of the developed sorbent for use in full-scale systems, such as constructed wetlands or the so-called filter/sorbent beds. These systems could be used as an alternative in rural areas and other places where traditional treatment methods cannot be applied.

Acknowledgements

This work was supported by the European Social Fund (ESF) under Grant (2014/0009/1DP/1.1.1.2.0/13/APIA/VIAA/044). The raw peat used in the present study was kindly provided by Silu kudra SIA (Latvia).

References

- [1] L. Zeng, X. Li, J. Liu, Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings, *Water Res.* 38 (2004) 1318–1326.
- [2] X. Song, Y. Pan, Q. Wu, Z. Cheng, W. Ma, Phosphate removal from aqueous solutions by adsorption using ferric sludge, *Desalination* 280 (2011) 384–390.
- [3] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), *Water Res.* 38 (2004) 4222–4246.
- [4] P. Loganathan, S. Vigneswaran, J. Kandasamy, N.S. Bolan, Removal and recovery of phosphate from water using sorption, *Crit. Rev. Environ. Sci. Technol.* 44 (2014) 847–907.
- [5] J.S. Cyrus, G.B. Reddy, Sorption and desorption of phosphorus by shale: Batch and column studies, *Water Sci. Technol.* 61 (2010) 599–606.
- [6] C.P. Vance, C. Uhde-Stone, D.L. Allan, Phosphorus acquisition and use: Critical adaptations by plants for securing a nonrenewable resource, *New Phytol.* 157 (2003) 423–447.
- [7] J.B. Xiong, Q. Mahmood, Adsorptive removal of phosphate from aqueous media by peat, *Desalination* 259 (2010) 59–64.
- [8] X. Yuan, C. Bai, W. Xia, B. Xie, J. An, Phosphate adsorption characteristics of wasted low-grade iron ore with phosphorus used as natural adsorbent for aqueous solution, *Desalin. Water Treat.* 54 (2015) 3020–3030.
- [9] C. Barca, C. Gérente, D. Meyer, F. Chazarenc, Y. André, Phosphate removal from synthetic and real wastewater using steel slags produced in Europe, *Water Res.* 46 (2012) 2376–2384.
- [10] Z. Yi, X. Shibin, K. Dandan, X. Dong, K. Lingwei, H. Feng, W. Zhenbin, Phosphorus removal from domestic sewage by adsorption combined photocatalytic reduction with red mud, *Desalin. Water Treat.* 51 (2013) 7130–7136.
- [11] C.H. Wang, S.J. Gao, T.X. Wang, B.H. Tian, Y.S. Pei, Effectiveness of sequential thermal and acid activation on phosphorus removal by ferric and alum water treatment residuals, *Chem. Eng. J.* 172 (2011) 885–891.
- [12] G. Lyngsie, O.K. Borggaard, H.C.B. Hansen, A three-step test of phosphate sorption efficiency of potential agricultural drainage filter materials, *Water Res.* 51 (2014) 256–265.
- [13] R. Giesler, T. Andersson, L. Lövgren, P. Persson, Phosphate sorption in aluminum- and iron-rich humus soils, *Soil Sci. Soc. Am. J.* 69 (2005) 77–86.
- [14] M.K. Wang, Y.M. Tzou, Phosphate sorption by calcite, and iron-rich calcareous soils, *Geoderma* 65 (1995) 249–261.
- [15] J.R. McLaughlin, J.C. Ryden, J.K. Syers, Sorption of inorganic phosphate by iron- and aluminum-containing components, *J. Soil Sci.* 32 (1981) 365–378.
- [16] C. Cocozza, V. D'Orazio, T.M. Miano, W. Shotyk, Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties, *Org. Geochem.* 34 (2003) 49–60.
- [17] S.A. Dean, J.M. Tobin, Uptake of chromium cations and anions by milled peat, *Resour. Conserv. Recycl.* 27 (1999) 151–156.
- [18] H. Joosten, D. Clarke, *Wise Use of Mires and Peatlands*, International Mire Conservation Group and International Peat Society, Saarijärvi, Finland, 2002.
- [19] O.R. Harvey, R.D. Rhue, Kinetics and energetics of phosphate sorption in a multi-component Al(III)-Fe

- (III) hydr(oxide) sorbent system, *J. Colloid Interface Sci.* 322 (2008) 384–393.
- [20] USEPA, Method 3050B: Acid Digestion of Sediment, Sludge and Soils. U.S. Governmental Printing Office, Washington, DC, 1996.
- [21] S. Lagergren, About the theory of so-called adsorption of soluble substances, *K. Sven. Vetenskapsakad. Handl.* 24 (1898) 1–39.
- [22] Y.S. Ho, G. McKay, Sorption of copper(II) from aqueous solution by peat, *Water Air Soil Pollut.* 158 (2004) 77–97.
- [23] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [24] Standard methods for the examination of water and wastewater, American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington, DC, 2005.
- [25] J. Murphy, J. Riley, A modified single solution method for the determination of phosphate in natural waters, *Anal. Chim. Acta* 27 (1962) 31–36.
- [26] F. Zucchini, M. Forte, A. Monac, M. De Bertoldi, Biological evaluation of compost maturity, *Biocycle* 22 (1981) 27–29.
- [27] D. Couillard, The use of peat in wastewater treatment, *Water Res.* 28 (1994) 1261–1274.
- [28] J. Livage, M. Henry, C. Sanchez, Sol-gel chemistry of transition metal oxides, *Prog. Solid State Chem.* 18 (1988) 259–341.
- [29] L. Anson, M. Klavins, L. Eglite, Use of peat-based sorbents for removal of arsenic compounds, *Cent. Eur. J. Chem.* 11 (2013) 988–1000.
- [30] I. Michalak, K. Chojnacka, A. Witek-Krowiak, State of the art for the biosorption process—A review, *Appl. Biochem. Biotechnol.* 170 (2013) 1389–1416.
- [31] N. Kuyucak, Biosorption of heavy metals, in: B. Volesky, CRC Press, Boca Raton, Florida, 1990, pp. 371–378.
- [32] B. Volesky, Detoxification of metal-bearing effluents: Biosorption for the next century, *Hydrometallurgy* 59 (2011) 203–216.
- [33] N.Y. Mezenner, A. Bensmaili, Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste, *Chem. Eng. J.* 147 (2009) 87–96.
- [34] Z.R. Holan, B. Volesky, Biosorption of lead and nickel by biomass of marine algae, *Biotechnol. Bioeng.* 43(11) (1994) 1001–1009.
- [35] T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Sargassum* seaweed as biosorbent for heavy metals, *Water Res.* 34 (2000) 4270–4278.
- [36] B. Volesky, H. May, Z.R. Holan, Cadmium biosorption by *Saccharomyces cerevisiae*, *Biotechnol. Bioeng.* 41 (1993) 826–829.
- [37] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, *Trends Biotechnol.* 16 (1998) 291–300.
- [38] D. Xu, J. Xu, J. Wu, A. Muhammad, Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems, *Chemosphere* 63 (2006) 344–352.
- [39] N. Bellier, F. Chazarenc, Y. Comeau, Phosphorus removal from wastewater by mineral apatite, *Water Res.* 40 (2006) 2965–2971.
- [40] N. Moelants, I.Y. Smets, J.F. Van Impe, The potential of an iron rich substrate for phosphorus removal in decentralized wastewater treatment systems, *Sep. Purif. Technol.* 77 (2011) 40–45.
- [41] N. Boujelben, J. Bouzid, Z. Elouear, M. Feki, F. Jamoussi, A. Montiel, Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents, *J. Hazard. Mater.* (2008) 103–110.
- [42] M. Aryal, M. Liakopoulou-Kyriakides, Equilibrium, kinetics and thermodynamic studies on phosphate biosorption from aqueous solutions by Fe(III)-treated *Staphylococcus xylosus* biomass: Common ion effect, *Colloids Surf., A* 387 (2011) 43–49.
- [43] Y. Su, H. Cui, Q. Li, S. Gao, J.K. Shang, Strong adsorption of phosphate by amorphous zirconium oxide nanoparticles, *Water Res.* 47 (2013) 5018–5026.
- [44] M.B. McBride, A critique of diffuse double layer models applied to colloid and surface chemistry, *Clays Clay Miner.* 45 (1997) 598–608.
- [45] J.C. Ryden, J.K. Syers, Rationalization of ionic strength and cation effects on phosphate sorption by soils, *J. Soil Sci.* 26 (1975) 395–406.
- [46] European Commission, Disposal and recycling routes for sewage sludge, Part 2—Regulatory report. Office for Official Publications of European Communities, Luxembourg, 2002. Available from: <http://ec.europa.eu/environment/archives/waste/sludge/pdf/sludge_disposal2.pdf>.
- [47] M. Vestberg, S. Kukkonen, K. Saari, T. Tuovinen, A. Palojarvi, T. Pitkanen, T. Hurme, M. Vepsäläinen, M. Niemi, Effects of cropping history and peat amendments on the quality of a silt soil cropped with strawberries, *Appl. Soil Ecol.* 42 (2009) 37–47.