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ORIGINAL ARTICLE

Removal of nickel(II) and lead(II) ions from aqueous solution using peat as a low-cost adsorbent: A kinetic and equilibrium study

Przemysław Bartczak, Małgorzata Norman, Łukasz Kłapiszewski,
Natalia Karwańska, Małgorzata Kawalec, Monika Baczyńska,
Marcin Wysokowski, Jakub Zdarta, Filip Ciesielczyk*, Teofil Jesionowski*

Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemical Technology and Engineering,
Berdychowo 4, PL-60965 Poznan, Poland

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Abstract Analysis was carried out to determine the physicochemical characteristics – morphological and structural, electrokinetic properties, elemental composition and functional groups – of peat, with a view to its use as a potential adsorbent of heavy metal ions from aqueous solutions. A significant part of the study comprised tests of adsorption of nickel(II) and lead(II) ions from model solutions. It was determined how the parameters of the adsorption process (time, pH, quantity of sorbent) influence the effectiveness of removal of nickel(II) and lead(II) ions. The adsorption kinetics are also described, using a pseudo-first-order model and pseudo-second-order models of types 1–4. The results show strong correspondence to a pseudo-second-order kinetics model of type 1 ($r^2 = 0.999$ for all initial concentrations). Another key part of the analysis was the use of the Langmuir and Freundlich models to determine the adsorption isotherms. The experimental data were in strong correspondence with Langmuir's isotherm model. The sorption capacities of peat with respect to nickel(II) and lead(II) ions were 61.27 mg(Ni²⁺)/g and 82.31 mg(Pb²⁺)/g.

* Corresponding authors. Tel.: +48 61 665 37 20; fax: +48 61 665 36 49 (T. Jesionowski). Tel.: +48 61 665 36 26; fax: +48 61 665 36 49 (F. Ciesielczyk).

E-mail addresses: Filip.Ciesielczyk@put.poznan.pl (F. Ciesielczyk), Teofil.Jesionowski@put.poznan.pl (T. Jesionowski).

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Desorption tests confirmed the possibility of reusing peat as an effective sorbent of environmentally harmful metals. A mechanism is also proposed for the adsorption of Ni^{2+} and Pb^{2+} ions on adsorbent.

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1. Introduction

Many branches of industry nowadays generate large quantities of waste containing toxic and carcinogenic organic and inorganic compounds. Particular attention needs to be paid to metal ions present in aqueous systems, including nickel(II) and lead(II) ions. When the permissible concentrations are exceeded, these ions exhibit toxic properties and a non-biodegradable character (Senthil Kumar et al., 2011; Saleh and Gupta, 2012; Jain et al., 2013).

The growing problem of water pollution has led to a great deal of interest in the development of innovative and relatively cheap methods of neutralizing such compounds. Methods generally used for this purpose are based on precipitation, membrane techniques, extraction, and adsorption (Ciesielczyk et al., 2013; Kołodyńska, 2013; Ouadjenia-Marouf et al., 2013; Rudnicki et al., 2014; Kłapiszewski et al., 2015). The last of these is considered to be one of the most effective ways of removing metal ions from aqueous solutions. An advantage of the adsorption process is its reversibility, by way of desorption, which enables the regeneration of the adsorbents used and recovery of the adsorbed compounds, including environmentally harmful metal ions (Naiya et al., 2009; Wawrzekiewicz and Hubicki, 2011; Senthil Kumar et al., 2012). An important factor determining the effectiveness of adsorption is the selection of appropriate process conditions, including the pH of the system, mass of sorbent, temperature and process time (Lourie and Gjengedal, 2011; Kowalczyk et al., 2013).

Over recent years numerous studies have been carried out, focusing on highly selective adsorbents of natural origin whose use does not generate further pollution. Increasingly often, studies are being made on substances which constitute waste material. The most frequently encountered adsorbents of metal ions include coconut shells, tree bark, zeolites, lignin, mollusc shells, citrus peel, minerals, natural clays and microorganisms (bacteria, fungi and yeast) (Öztürk, 2007; Guo et al., 2008; Wang and Peng, 2010; Kołodyńska et al., 2012; Rao and Kashifuddin, 2012; Inagaki et al., 2013; Singha and Das, 2013; Şahin et al., 2013; Ghorbel-Abid and Trabelsi-Ayadi, 2015; Lim and Lee, 2015). It is notable that natural materials have distinct sorption properties depending on the location where they are found. This means that biosorbents are still innovative materials which have not yet been completely studied and characterized.

Peat is one of the natural sorbents which can be ascribed to this group of materials (Sòukand et al., 2002; Liu et al., 2008; Balasubramanian et al., 2009; Xiong and Mahmood, 2010; Lattuada et al., 2014; Zehra et al., 2015). Owing to its wide availability and low extraction cost, it is regarded as a low-cost adsorbent, which is favourable for the development of low-cost neutralization technologies for waste and impurities. Peat is made up of a complex mixture of organic compounds,

which include organic acids (humic and fulvic) and their salts, as well as cellulose, lignin and proteins, along with mineral components (magnesium, potassium, calcium, sodium, iron, silicon and aluminium). This composition leads to very good sorption properties, linked to the presence on the surface of acid functional groups (carboxyl $-\text{COOH}$, phenolic $-\text{OH}$, sulphonic $-\text{SO}_3\text{H}$), which enable the exchange of H^+ ions for other cations (Brown et al., 2000).

In the present study, peat (obtained from the village of Leszno on the river Ner in Poland) was investigated as a potential adsorbent of nickel(II) and lead(II) ions. There is no information in the literature concerning the use of peat originating from this type of geographical location, a fact which confirms without doubt the novelty of this work. As part of the study, the basic parameters for carrying out of the adsorption process were determined. The kinetics of the adsorption of the aforementioned ions on peat were investigated using pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho and McKay, 1999) models, and the adsorption isotherms were found using the models of Freundlich (1906) and Langmuir (1918). Another significant part of the study was the performance of desorption tests for the purpose of regeneration of the sorbent.

2. Experimental

2.1. Preparation of peat as a natural adsorbent

The studied peat was mechanically excavated from a peatland located in the village of Leszno, near the Ner river (Poland, GPS coordinates $52^{\circ}5'N$, $18^{\circ}56'E$). It was dried at 105°C for 24 h, then refined and classified. Peat prepared in this way was tested as a potential adsorbent of Ni(II) and Pb(II) ions.

The peat used as an adsorbent was subjected to thorough physicochemical analysis. The dispersive-morphological character of the material was determined on the basis of SEM images and particle size distribution using a Mastersizer 2000 analyser (Malvern Instruments Ltd., UK). This instrument uses the laser diffraction method, and its measuring range is from 0.2 to 2000 μm . The SEM images were recorded with a scanning electron microscope (Zeiss EVO40, Germany). The electrokinetic properties of the peat were also established. First, electrophoretic mobility was measured at a constant ionic force of 0.001 M NaCl, and then the zeta potential was calculated using the Henry equation (Zetasizer Nano ZS equipped with an autotitrator – Malvern Instruments Ltd., UK). Its elemental composition was determined using the Vario El Cube system (Elementar Analysensysteme GmbH, Germany), and its FT-IR spectrum was evaluated using an EQUINOX 55 spectrophotometer (Bruker, Germany), so that the functional groups present on the peat surface could also be identified. The materials were analysed in the form of tablets,

made by pressing a mixture of anhydrous KBr (ca. 0.1 g) and 1 mg of the tested substance in a special steel ring under a pressure of approximately 10 MPa. The investigation was performed over a wavenumber range of 4000–400 cm^{-1} (at a resolution of 0.5 cm^{-1}). The aforementioned methods enabled the full characterization of peat as an adsorbent of natural origin. The sorption properties were determined by plotting the nitrogen adsorption/desorption (at 77 K) isotherms, and indirectly by finding the surface area and total volume as well as mean size of pores. Such parameters as specific surface area (A_{BET}), size distribution (S_p) and volume (V_p) of pores were obtained by making a precise analysis of the adsorption/desorption isotherms in stationary conditions and using the BET and BJH algorithms. These measurements were performed using an ASAP 2020 apparatus (Micromeritics Instruments Co., USA).

2.2. Batch adsorption studies

The adsorption process was carried out using inorganic salts as metal ion precursors. The precursor of nickel(II) ions was nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; POCh SA), and the precursor of lead(II) was lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$; POCh SA). Model solutions were prepared with concentrations in the range 15–100 mg/L. An important part of the study was the determination of optimum conditions for carrying out the process of removing metal ions (Table 1). The effect of the following factors was investigated: time of contact between adsorbate and adsorbent (1–240 min), pH of the system (1–9), and mass of sorbent (0.5–5 g).

Prepared solutions of salts in the appropriate concentrations were placed in conical flasks, and the appropriate quantity of adsorbent was added. The system was then mixed using a magnetic stirrer (Ika Werke GmbH, Germany) over suitable time intervals. The resulting mixture was filtered under reduced pressure (Sartorius, Germany). The product was dried for 24 h at 105 °C. To determine the effectiveness of the adsorption process, further analysis was carried out on the filtrate obtained at each stage of adsorption. The effectiveness of adsorption was estimated with the use of atomic absorption spectrometry (AAS) applying a Z-8200 spectrometer equipped with premix fishtail type burner – air/acetylene and N_2O /acetylene, graphite furnace – flame and furnace on the same beam made by Hitachi, Japan, this being one of the most accurate methods of quantitative analysis for measuring nickel(II) and lead(II) ion (the wavelength for the determination of Ni is

232.0 nm and 283.3 nm for Pb) concentrations in the filtrate following adsorption. The adsorption process was also carried out over a wide pH range.

The effectiveness of adsorption of metal ions on natural peat was determined using the following formula (1):

$$\text{removal } \% = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

where C_o and C_e are respectively the initial and equilibrium concentrations of nickel(II) or lead(II) ions (mg/L).

The kinetics of the process of adsorption of nickel(II) and lead(II) ions were also determined. For this purpose, adsorption was carried out using 0.5 g of peat and 100 mL of solutions of nickel(II) and lead(II) in different concentrations (15–100 mg/L), over different time intervals (1–240 min). The residual concentrations of nickel(II) and lead(II) ions in the solution were determined using AAS analysis. The quantity of metal ions adsorbed in unit time q_t was calculated from the following formula (2):

$$q_t = \frac{(C_o - C_t) \cdot V}{m} \quad (2)$$

where C_o and C_t are the concentrations of nickel(II) or lead(II) ions in the solution before and after sorption (mg/L), V is the volume of the solution (L), and m is the mass of peat (g).

To determine the adsorption isotherms it was necessary to find the equilibrium concentration (q_e) of adsorbed metal ions on natural peat. The equilibrium concentration (q_e) was determined using the following formula (3):

$$q_e = \frac{(C_o - C_e) \cdot V}{m} \quad (3)$$

where q_e is the quantity of metal ions adsorbed at equilibrium (mg/g), and C_e is the equilibrium metal ion concentration (mg/L).

2.3. Desorption studies

Desorption of nickel(II) or lead(II) ions from the spent peat was carried out with varying concentrations of HCl solution (0.05–0.1 M). The spent peat (0.5 g) was placed in a beaker with 100 mL of hydrochloric acid in the appropriate concentration, and the system was then mixed using a magnetic stirrer (Ika Werke GmbH, Germany) for 60 min. The resulting mixture was filtered under reduced pressure using specialized equipment and filters (Sartorius, Germany). The filtrate was analysed using AAS to determine the degree of desorption of metal ions from the peat.

All measurements of adsorption as well as desorption test were repeated three times. The presented values are averaged.

3. Results and discussion

3.1. Physicochemical characteristics of peat

Elemental analysis provided information about the chemical composition of the peat sample, giving the content of carbon as 47.1%, hydrogen 6.4%, nitrogen 2.8%, and sulphur 0.9%. The peat also contains a considerable amount of oxygen, whose content was indirectly determined as approximately 27.0%.

Table 1 Process conditions for the removal of nickel(II) and lead(II) ions by natural peat.

Optimized parameter	Adsorption process conditions
Time (1, 3, 5, 10, 15, 30, 45, 60, 90, 120, 180 and 240 min)	Initial metal ion concentration: 15, 30, 50 and 100 mg/L; mass of peat = 0.5 g; pH = 5
pH (1, 3, 5, 7 and 9)	Initial metal ion concentration: 15, 30, 50 and 100 mg/L; mass of peat = 0.5 g; time = 60 min
Mass of peat (0.5, 1, 2, 3, 4, 5 g)	Initial metal ion concentration: 50 mg/L; time = 60 min; pH = 5

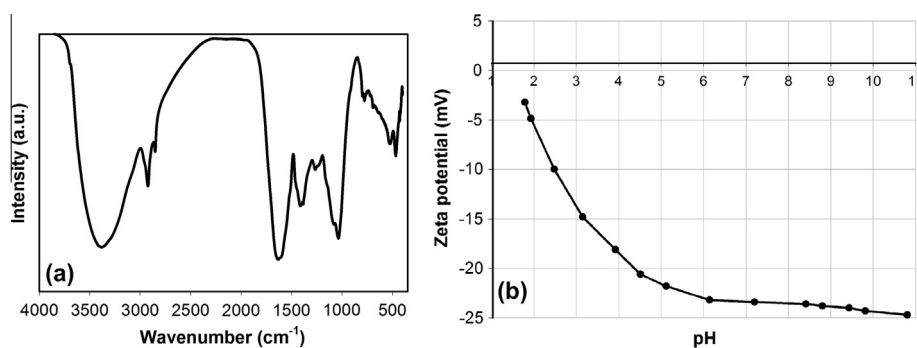
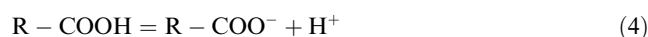


Figure 1 FT-IR spectrum (a) and zeta potential vs. pH (b) of peat sample.

Analysis of the FT-IR spectrum of natural peat (Fig. 1A) confirmed the presence of functional group characteristic of peat. Hydroxyl groups were identified by the broad band attributed to stretching vibrations of O—H bonds in the range 3600–3100 cm^{-1} , while additionally ether groups were manifested by the band attributed to stretching vibrations of C—O bonds at 1100–1000 cm^{-1} , carbonyl groups by the band attributed to stretching vibrations of C=O bonds at 1750–1500 cm^{-1} and signal at 1413 cm^{-1} is associated with the stretching vibrations of C—OH groups in the structure of peat. The presence of a developed aliphatic structure is confirmed by the absorption band attributed to the stretching vibrations of C—H bonds in the range 2980–2840 cm^{-1} . The bands originating from the bonds of the aromatic structure may overlap with those attributed to the bonds of other groups. In general, the FT-IR spectrum confirms the diversity of the peat's structural composition. The detailed analysis of the peat is consistent with the data given by León-Torres et al. (2012). The presence of such a variety of functional groups on the peat surface makes it an attractive adsorbing material.

Fig. 1B shows the zeta potential as a function of pH, recorded for a peat sample. The measurements were made in a 0.001 M solution of NaCl. The character of the obtained electrokinetic curve suggests that the zeta potential of peat strongly depends on the pH. For the analysed peat sample the zeta potential values were negative over the whole investigated pH range, namely for pH from 1.7 to 11, where the electrokinetic potential varied from -3 to -25 mV. These zeta potential values are in agreement with the data presented by Asadi et al. (2011a,b), who reported that the zeta potential of peat varied from 2.4 to -23 mV. The initial pH of peat, at which the zeta potential is -23 mV, is 6.7. With increasing

pH the zeta potential becomes increasingly negative. Peat usually has a negative surface charge, which is attributed to the negative charge of organic functional groups resulting from the dissociation of H^+ ions according to Eq. (4):



The zeta potential of peat particles in colloidal systems has also been found to depend significantly on the concentration and type of the electrolyte (Asadi et al., 2011a,b; Moayedi et al., 2011). The electrokinetic curve of the peat sample used in this study did not reach the isoelectric point (i.e.p.); however, its shape suggests that such a point would be reached at a pH of about 1.3. It can be concluded that peat demonstrates rather good electrokinetic stability in the alkaline pH range.

The parameters of porous structure of the peat sample were also determined, using the BET method. It was found that, in spite of its good sorption properties, the specific surface area of peat as a natural sorbent is small, amounting to 1.40 m^2/g . The total pore volume of the peat is 0.01 cm^3/g , while the average pore size is 14.6 nm.

Information about the peat's dispersion, grain morphology and character of agglomeration was obtained from the particle size distribution diagram according to the volume contribution (Fig. 2A) and SEM image (Fig. 2B).

The studied peat sample was found to contain 10% particles with diameters smaller than 4.4 μm , 50% particles with diameters smaller than 31.5 μm , and 90% particles with diameters smaller than 118.1 μm . The mean particle diameter in the whole volume of the peat sample $D[4.3]$ is 49.1 μm . The SEM image confirms the dominance of particles with large diameter and irregular shape.

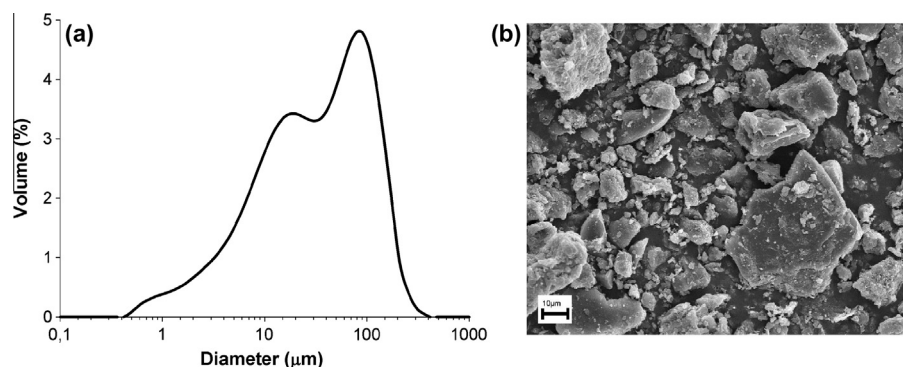


Figure 2 Particle size distribution according to volume contribution (a) and SEM image (b) of the peat.

Based on the physicochemical analysis it can be concluded that the peat offers good possibilities for application as a potential adsorbent of metal ions.

3.2. Adsorption process

3.2.1. Effect of contact time

In the first stage of the study, it was determined how the time of contact between sorbent and adsorbate (with concentrations of nickel(II) and lead(II) ions in the range 15–100 mg/L) affects the quantity of metal ions adsorbed in a given time interval (q_t). The experimental data obtained are shown in Fig. 3a and b.

The results show that a state of equilibrium of the adsorption of nickel(II) ions on natural peat is reached after just 15 min for the lowest concentration of model solution (15 mg/L), and after 30 min for the other concentrations (30, 50 and 100 mg/L). The highest effectiveness of the process was attained after 60 min. In the case of adsorption of lead (II) ions, adsorption equilibrium is reached after 3 min for ion concentrations of 15 and 30 mg/L, after 5 min for 50 mg/L, and after 15 min for 100 mg/L.

Verification of the results obtained clearly indicates the effectiveness of the process of adsorption of nickel(II) or lead(II) ions from the model aqueous solutions using a material of natural origin. In the case of adsorption of Pb(II) ions from model solutions with concentrations of 15–100 mg/L, a process effectiveness in the range 98.9–100% was obtained. Irrespective of the adsorption time, a higher effectiveness was obtained for the removal of lead(II) ions. This may indicate that the surface of peat has a greater affinity for ions of that metal. The dependences obtained are related to different degrees of hydration of metal ions precursors ($\text{Pb}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). The higher degree of metal ion hydration, the more difficult adsorption due to difficult access to the peat surface, and consequently the lower degree of its removal. Moreover, lead atom is bigger than nickel one, which also influences its uptake from aqueous solutions. The electrons are easily polarized and to a lower degree retained by the nucleus (better match of the radius of metal ion, and also the symmetry of its electron orbital). It was also confirmed by other scientists (Kalmykova et al., 2008). The computed values for the quantity of nickel(II) or lead(II) ions adsorbed vs. time (t), q_t (mg/g), were also used when determining the kinetics of the adsorption process.

3.2.2. Effect of pH

A very important parameter in the process of adsorption of nickel(II) and lead(II) ions is the pH of the reaction system. This applies particularly to peat, a sorbent of natural origin whose surface contains numerous acid functional groups. Manipulation of the pH of the system may cause dissociation of these groups and bring about a significant improvement or worsening of the effectiveness of removal of nickel(II) and lead (II) ions from model solutions.

It was determined how pH (in the range 1–9) influences the effectiveness of removal of nickel(II) and lead(II) ions from model aqueous solutions using peat as a natural adsorbent. The effect of pH values in the acidic (pH = 1, 3, 5), neutral (pH = 7) and alkaline (pH = 9) ranges was determined for a metal ion concentration equal to 50 mg/L. The results, shown in Fig. 4a, imply that the pH of the aqueous system has a significant impact on the effectiveness of the process. The effectiveness of adsorption of nickel(II) ions from model solutions with a concentration of 50 mg/L increases as the system becomes more alkaline. For both nickel(II) and lead(II) ions, the lowest effectiveness (42.7% and 63.1% respectively) was obtained when the process took place in the most acidic environment (pH = 1). The greatest effectiveness for model solutions containing Ni(II) ions (92.5%) was obtained in the most alkaline environment (pH = 9). In the case of adsorption of lead(II) ions the greatest effectiveness was recorded at pH = 5, and attained 100%. Irrespective of the pH of the reaction system, the effectiveness of the process was found to be significantly greater in the case of adsorption of lead(II) ions. This may indicate that the surface of peat has a greater affinity for lead(II) ions than for nickel(II) ions, as has also been confirmed by other researchers in studies in which Sphagnum peat was used (Kalmykova et al., 2008).

The effectiveness of removal of nickel(II) and lead(II) ions using peat as a natural adsorbent increased as the system became more alkaline. This result is explained by the presence of acid functional groups on the peat surface. At low pH values (1–3) there are no changes in their properties; their binding properties are modified only when the pH of the system is increased, due to the dissociation of hydrogen from the acid functional groups. This may explain to a large extent the mechanism of the adsorption process as proposed in a later chapter. Besides this, the pH = 5 is optimal value for adsorption of both metal ions (nickel(II) and lead(II)) – there is no precipitation of metal hydroxides. Comparison of pH influence on the

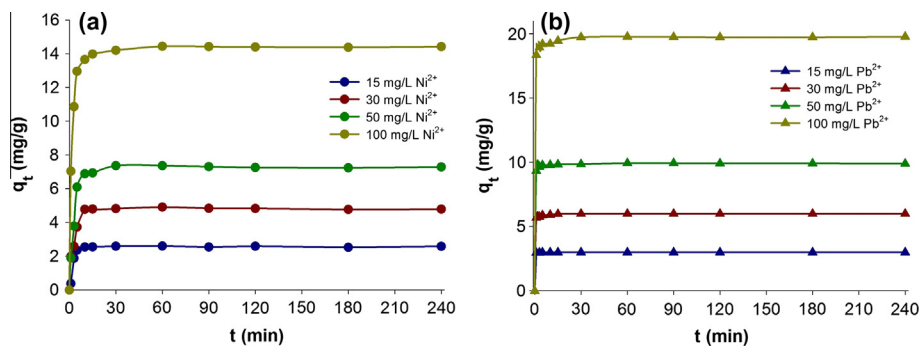


Figure 3 Effect of contact time on the removal of nickel(II) (a) and lead(II) (b) ions by peat (metal ion concentration 15–100 mg/L, peat dose 0.5 g, volume of sample 100 mL, time 1–240 min).

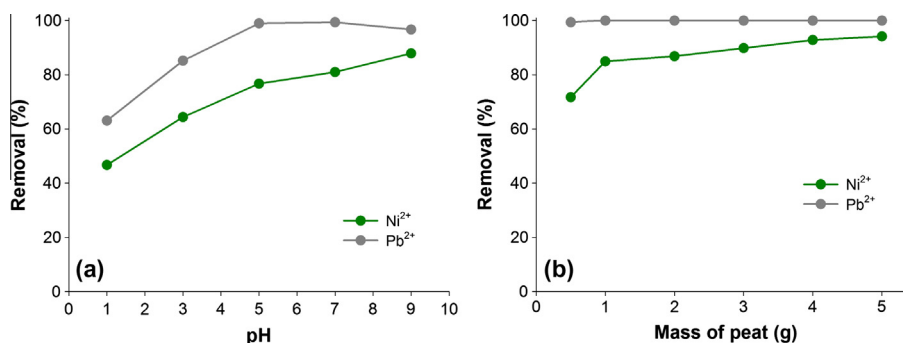


Figure 4 Effect of pH (a) and adsorbent dose (b) on the removal of nickel(II) and lead(II) ions by peat.

Table 2 pH optimum adsorption of selected metal ions with the use of peat.

Metal adsorbed	Optimal pH	Reference
Ni ²⁺ , Pb ²⁺	5.0–7.0	This study
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	6.0	Qin et al. (2006)
Cu ²⁺ , Ni ²⁺ , Cd ²⁺	6.0–7.0	Liu et al. (2008)
Pb ²⁺	5.5	Zehra et al. (2015)
Cu ²⁺ , Pb ²⁺ , Cd ²⁺	5.0–6.5	Villaverde et al. (2009)

adsorption of different types of metal ions onto peat is presented in Table 2. Collected information confirms that the optimum pH of the process is not higher than 6.0 to avoid the precipitation of metal hydroxides. According to the Pourbaix diagram above pH 7.5 may precipitate forms hydroxyl metals.

3.2.3. Effect of adsorbent dose

The peat dose is an very important parameter for the quantitative removal of nickel(II) and lead(II) ions from model wastewater. Optimization of the mass of sorbent used was performed for a model solution concentration of 50 mg/L. The process was carried out for 60 min for different masses of sorbent in the range 0.5–5 g.

The graphs in Fig. 4b show a comparison of the effectiveness of removal of nickel(II) and lead(II) ions from model solutions of concentration 50 mg/L. In the case of nickel(II) ions the effectiveness of the adsorption process increased with an increase in the mass of sorbent. The lowest value obtained was 79.8%, when 0.5 g of peat was used. The greatest effectiveness (94.2%) was obtained when 5 g of peat was used. For the adsorption of lead(II) ions the effectiveness was 100% when the sorbent was used in quantities of 1–5 g. A minimal difference in the adsorption of ions of that metal was observed when the mass of sorbent was 0.5 g – here the effectiveness was 99.4%.

This effect is due to the increase in the surface area of the sorbent, as has also been confirmed in other studies (Amarasinghe and Williams, 2007; Ibrahim et al., 2012).

3.3. Adsorption kinetics

When adsorption is used for the removal of selected metal ions, it is particularly important to determine the process kinetics, which may facilitate the design of the process in real-life conditions. Kinetics models based on the quantity of

substance adsorbed as a function of time have been proposed in other work (Vasanth Kumar and Sivanesan, 2006; Areco et al., 2013). In this study, to determine the rate and mechanism of the process of adsorption, the pseudo-first-order kinetics model of Lagergren (1898) and the pseudo-second-order model of Ho and McKay (1999) were used.

3.3.1. Lagergren pseudo-first-order kinetics model

In a kinetics model of Lagergren's pseudo-first-order type, the rate of reaction is directly proportional to the difference between the equilibrium concentration of adsorbate in the solid phase of the adsorbent and the momentary concentration in the solid phase. The Lagergren pseudo-first-order model can be expressed by Eq. (5) (Lagergren, 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

where q_e and q_t (mg/g) are the quantities of metal ions adsorbed at equilibrium and at time t (min) respectively, and k_1 (1/min) is the rate constant for the pseudo-first-order rate equation.

After integration and application of the boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$), Eq. (5) can be rewritten for linearized data plotting in the form (6):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (6)$$

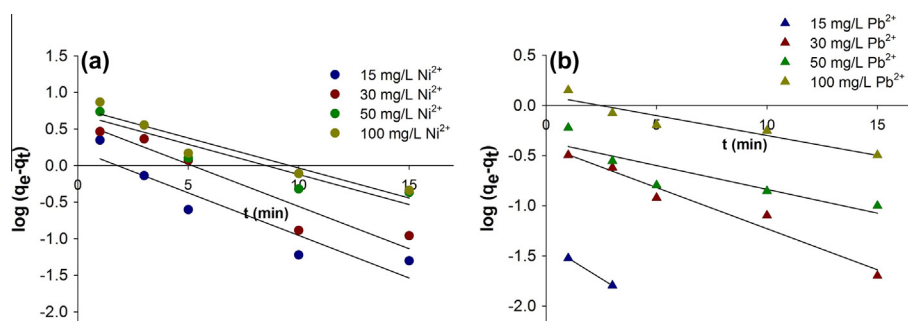
The equilibrium adsorption capacity (q_e) and adsorption rate constant (k_1) (Table 3) were computed experimentally from the graph of $\log(q_e - q_t)$ versus t , which is shown in Fig. 5.

Table 3 shows the computed values of the adsorption rate constant (k_1) for particular concentrations of metal ions, calculated from the gradients in Fig. 5. The correlation coefficient (r^2) computed for the pseudo-first-order model of adsorption of nickel(II) ions lay within the range 0.689–0.874, while for the adsorption of lead(II) ions the range was 0.669–1.000 for the concentrations used. This indicates that the pseudo-first-order kinetics model fits fairly well to the experimental data obtained in the case of adsorption of lead(II) ions (model solution concentrations 15, 30, 100 mg/L). This is because in the case of the model solution concentrations of lead(II) ions, a state of adsorption equilibrium was attained quickly. Nonetheless the results for the quantity of adsorbed metal ions over time ($q_{e,cal}$) computed from the pseudo-first-order kinetics model of adsorption deviated markedly from the experimental values ($q_{e,exp}$). It should also be noted that for lead(II) ions in

Table 3 Pseudo-first-order and pseudo-second-order types 1–4 kinetics parameters and coefficient of determination for the adsorption of nickel(II) and lead(II) ions onto peat.

Type of kinetics model	Parameter	Unit	Initial concentration of Ni ²⁺ (mg/L)				Initial concentration of Pb ²⁺ (mg/L)				
			15	30	50	100	15	30	50	100	
	$q_{e,exp}$	mg/g	2.610	4.910	7.370	14.440	3.000	6.000	9.940	19.780	
Pseudo-first-order	$q_{e,cal}$	mg/g	0.827	1.780	5.036	3.860	0.041	1.593	0.878	4.488	
	k_1	1/min	0.164	0.126	0.190	0.108	0.314	-1.054	-1.313	-3.145	
	r^2	–	0.869	0.689	0.874	0.812	1.000	0.964	0.669	0.973	
Pseudo-second order	Type 1	$q_{e,cal}$	mg/g	2.580	4.813	7.327	14.460	3.000	6.003	9.913	19.781
		k_2	g/mg min	0.807	0.366	0.122	0.069	79.491	2.282	3.677	0.051
		h	mg/g min	5.374	8.488	6.529	14.460	715.461	82.239	361.337	19.783
		r^2	–	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	Type 2	$q_{e,cal}$	mg/g	2.778	4.888	8.083	14.808	3.001	5.986	9.905	19.659
		k_2	g/mg min	0.205	0.131	0.039	0.062	31.207	2.727	1.611	0.649
		h	mg/g min	1.582	3.137	2.526	13.629	281.045	97.706	158.078	250.938
		r^2	–	0.972	0.925	0.982	0.992	0.919	0.860	0.971	0.871
	Type 3	$q_{e,cal}$	mg/g	2.800	6.525	-7.530	22.355	1.418	5.996	9.908	19.696
		k_2	g/mg min	0.196	0.139	0.014	0.011	-62.714	2.337	1.564	0.563
		h	mg/g min	1.538	1.809	0.799	5.416	-126.167	84.011	153.505	218.546
		r^2	–	0.972	0.874	0.927	0.997	0.213	0.860	0.971	0.871
Type 4	$q_{e,cal}$	mg/g	2.761	5.067	8.030	14.784	3.002	5.995	9.910	19.688	
	k_2	g/mg min	0.215	0.105	0.040	0.063	28.462	2.325	1.551	0.563	
	h	mg/g min	1.639	2.706	2.600	13.809	256.433	83.580	152.328	218.170	
	r^2	–	0.870	0.854	0.841	0.974	0.917	0.852	0.968	0.862	

The bold values are related with the parameters of the pseudo-second order kinetic model of type 1 which preferably describe realized process of adsorption as compared to bold experimental data.

**Figure 5** Pseudo-first-order kinetics fit for the adsorption of nickel(II) (a) and lead(II) (b) ions onto peat.

concentrations of 30, 50 and 100 mg/L a negative value of k_1 (the adsorption rate constant) was obtained. A much better fit was obtained using the pseudo-second-order model, as will be described in the following section.

3.3.2. Ho pseudo-second-order kinetics model

In Ho's pseudo-second-order kinetics model, the rate of the adsorption process is assumed proportional to the square of the difference from the equilibrium concentration of adsorbate. This model is represented by Eq. (7) (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

where k_2 (g/(mg min)) is the rate constant for the pseudo-second-order rate equation, and q_e and q_t are the quantities (mg/g) of ions adsorbed at equilibrium and at time t (min).

When the boundary conditions are introduced, Eq. (7) takes the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The initial adsorption rate h (mg/(g min)) is defined as follows:

$$h = k_2 q_e^2 \quad (9)$$

The values of k_2 and q_e can be determined from the gradient and intercept, respectively, of the plot of t/qt vs. t . This relationship can be classified as a pseudo-second-order kinetics model of type 1.

It should also be born in mind that k_2 and q_e can be calculated from the plots for the linear forms of equations given in Table 4 as pseudo-second-order kinetics models of types 1–4 (Vasanth Kumar and Sivanesan, 2006). The values of k_2 , h

Table 4 Linear forms of pseudo-second-order kinetics model.

Type of kinetics pseudo-second order	Linear form	Plot
Type 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ vs. t
Type 2	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{q_t}$ vs. $\frac{1}{t}$
Type 3	$\frac{1}{t} = \frac{k_2 q_e^2}{q_t} - \frac{k_2 q_e^2}{q_e}$	$\frac{1}{t}$ vs. $\frac{1}{q_t}$
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - \frac{k_2 q_e^2}{q_e}$	$\frac{q_t}{t}$ vs. q_t

and $q_{e,cal}$ obtained from the four linear forms of pseudo-second-order equations were found to be different.

The kinetics of the adsorption of nickel(II) and lead(II) ions from model solutions of concentrations 15, 30, 50 and 100 mg/L onto natural peat was relatively well-described using the pseudo-second-order kinetics model of type 1. Pseudo-second-order models of types 2–4, in spite of the high values of their correlation coefficients, cannot be taken into consideration because of the large differences between the experimental and calculated sorption capacities.

In the case of the pseudo-second-order kinetics model of type 1, the coefficient of correlation (r^2), calculated from the slopes of the curves shown in Fig. 6a, was 0.999, for adsorption of both nickel(II) and lead(II) ions, irrespective of their concentration in the model solution. It should also be noted that the quantities of adsorbed metal ions ($q_{e,cal}$) computed from the pseudo-second-order kinetics model of type 1 corresponded very well with the experimental data ($q_{e,exp}$). The

initial adsorption rate (h) was not found to have any tendency to increase with increasing concentration; this may be related to the heterogeneity of the natural material.

For pseudo-second-order kinetics models of types 2 and 3 (Figs. 6b and 7a) the correlation coefficient lies in the range 0.874–0.997 for adsorption of nickel(II) ions, and in the range 0.213–0.971 for adsorption of lead(II) ions. The adsorption capacities ($q_{e,cal}$) computed from the pseudo-second-order kinetics models of types 2 and 3 did not fit with the experimental capacities ($q_{e,exp}$) to the same degree as in the case of the model of type 1. Also the values of the adsorption rate constant (k_2) and initial adsorption rate (h) obtained using the type 3 model for a lead ion concentration of 15 mg/L were found to be negative. The parameters computed using the pseudo-second-order models of types 2 and 3 indicate that these models cannot be used to describe properly the kinetics of the process of adsorption of nickel(II) and lead(II) ions on natural peat.

The pseudo-second-order kinetics model of type 4 (Fig. 7b, Table 3) produced unfavourable results. This is confirmed by the low value of the coefficient of correlation (r^2), which lies in the range 0.841–0.974 for various initial concentrations of nickel(II) ions, and 0.852–0.968 for lead(II) ions. The coefficients of correlation (r^2) obtained using the pseudo-second-order kinetics model of type 4 are markedly lower than those obtained using the type 1 model.

To sum up the results concerning the adsorption kinetics, it can be concluded that the pseudo-second-order kinetics model provides a significantly better description of the kinetics of the adsorption of nickel(II) and lead(II) ions on natural peat.

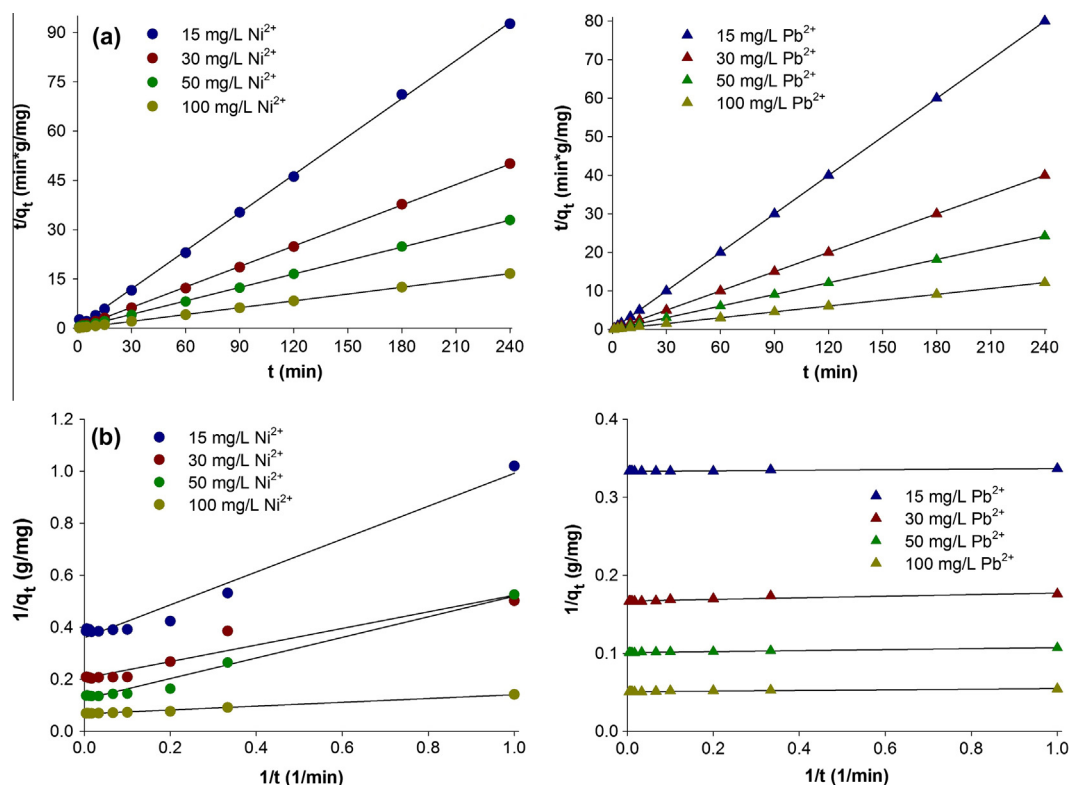


Figure 6 Types 1 (a) and 2 (b) pseudo-second-order kinetics model, obtained using a linear method, for the adsorption of Ni^{2+} and Pb^{2+} on peat.

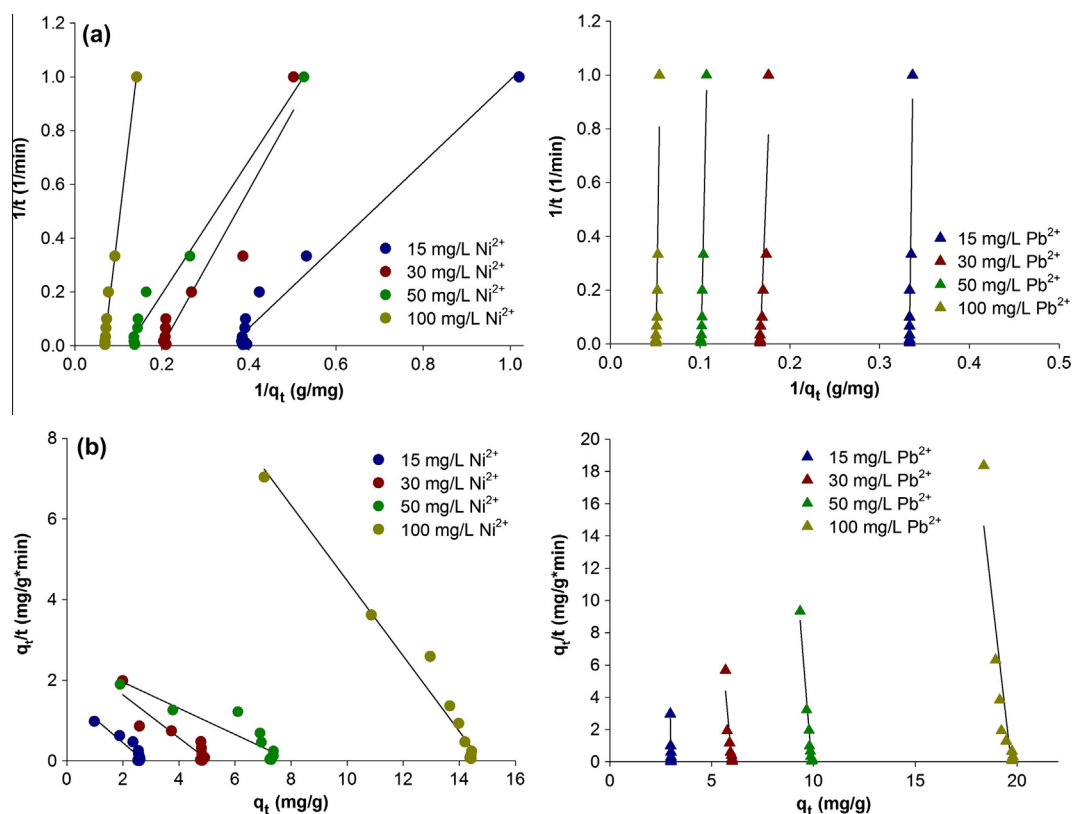


Figure 7 Types 3 (a) and 4 (b) pseudo-second-order kinetics model, obtained using a linear method, for the adsorption of Ni^{2+} and Pb^{2+} on peat.

3.4. Adsorption isotherms

Adsorption isotherms describe the relationship between the quantity of substance adsorbed and the concentration in the equilibrium solution. An important element of the implementation of a metal ion adsorption process is the fitting of experimental data to an appropriate adsorption isotherm model. Analysis of the adsorption isotherms obtained provides much valuable information about the mechanism and nature of the adsorption process. Fig. 8 shows the plot of q_e versus C_e for the adsorption isotherms of nickel(II) and lead(II) on peat at 25 °C. The experimental data were applied to the three-parameter isotherm models of Freundlich (1906) and Langmuir (1918). Table 4 gives the coefficient of correlation, the parameters of the adsorption equation and the quantity of metal ions adsorbed at equilibrium concentration (q_e).

3.4.1. Langmuir adsorption isotherms

Langmuir's isotherm model is based on a theory of monolayer adsorption. The quantity of particles adsorbed corresponds to the number of active centres on the surface of the adsorbent. Based on the assumptions described below, the equation of Langmuir's isotherm model takes the following form (10):

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (10)$$

where q_m is the maximum uptake of nickel(II) or lead(II) ions (mg/g), and K_F (L/mg) is the adsorption equilibrium constant.

The values of b and q_m (which are listed in Table 4) can be estimated from the intercept and gradient of the linear plot of C_e/q_e vs. C_e .

Langmuir's isotherm model can be characterized using a dimensionless separation factor (R_L), which can be computed from (11):

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (11)$$

where C_0 is the initial concentration of nickel(II) or lead(II) ions (mg/L).

3.4.2. Freundlich adsorption isotherms

Freundlich's isotherm model is most often used to describe a process of adsorption taking place on adsorbents with a heterogeneous structure. The model is described by following Eq. (12):

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (12)$$

where K_F is the Freundlich constant related to the bonding energy (L/g), and n is an empirical constant characterizing the heterogeneity of the process (g/L). According to the Freundlich model assumptions, if $n < 1$ the adsorption process is unfavourable, while if $1 < n < 10$, the adsorption process is favourable.

The Freundlich constants K_F and n can be calculated from the intercept and gradient of the plot between $\log q_e$ and $\log C_e$.

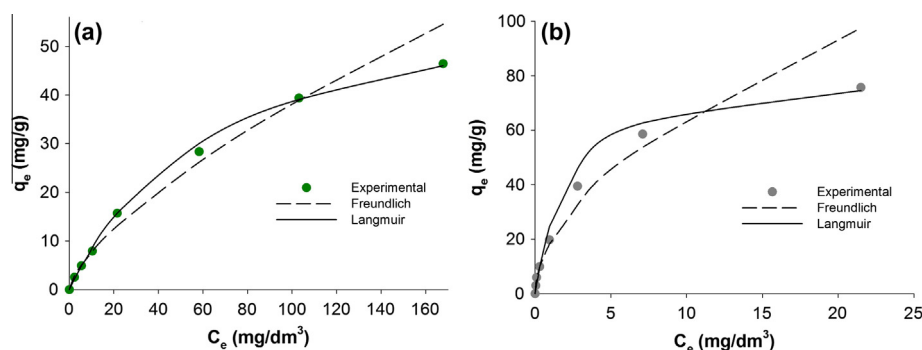


Figure 8 Fitting of the Langmuir and Freundlich isotherm models to equilibrium results for nickel(II) (a) and lead(II) (b) ions adsorbed onto peat.

3.4.3. Comparison of adsorption isotherms

The results obtained concerning the adsorption of Ni^{2+} and Pb^{2+} ions from aqueous solution are presented in Table 5. Fig. 8 shows the equilibrium adsorption isotherm and fitting of the models to experimental data. At low concentrations of adsorbate the process is very rapid, indicating high affinity towards the solute. At higher concentrations of nickel(II) or lead(II) the quantity of metal ions adsorbed increases very slightly, making an almost horizontal plateau.

Confirmation of experimental data fit to the Langmuir isotherm model is high value of correlation coefficients (r^2) were in the range 0–1, which confirmed that the sorption of nickel(II) and lead(II) ions was favourable ($R_L > 1$). The maximum sorption capacities were 61.27 $\text{mg}(\text{Ni}^{2+})/\text{g}$ and 82.31 $\text{mg}(\text{Pb}^{2+})/\text{g}$. Peat was found to have significantly better sorption properties with respect to Pb^{2+} . A comparison with maximum monolayer adsorption capacities for nickel(II) or lead(II) ions on other adsorbents is presented in Table 6.

Comparing the sorption capacity of the peat used with that of other materials serving as low-cost adsorbents, it is found that the present study produced very favourable results. It should be noted that the sorption properties of adsorbents of plant origin are conditioned to a large degree by geographical location. Peat which originates from Poland possesses significantly higher adsorptive capacity in comparison with the one coming from other countries.

Application of the Freundlich isotherm model produced coefficients of correlation (r^2) equal to 0.986 for Ni^{2+} and 0.525 for Pb^{2+} . This shows that in the case of adsorption of Pb(II) ions, the model is poorly fitted to the experimental data. The value $1/n$, in the case of adsorption of both Ni(II) and Pb

Table 6 Comparison of adsorption capacity of Ni(II) and Pb(II) ions by low-cost adsorbents.

Metal adsorbed	Adsorbent type	q_m (mg/g)	Reference
Ni^{2+}	Peat	61.27	This study
	Wheat straw	41.84	Dhir and Kumar (2010)
	Barley straw	35.80	Thevannan et al. (2010)
	Tea factory waste	18.42	Malkoc and Nahoglu (2005)
	Peat (Brazil)	14.00	Lattuada et al. (2014)
	Peat (Ireland)	11.42	Liu et al. (2009)
	Orange peel	9.80	Feng et al. (2011)
	Jute fibres	4.23	Shukla and Pai (2005)
Pb^{2+}	Peat	82.31	This study
	Peat (Indonesian)	79.68	Balasubramanian et al. (2009)
	Tree fern	40.00	Ho et al. (2004)
	Hyacinth roots	24.94	Singha and Das (2012)
	Coconut shell	24.24	Singha and Das (2012)
	Rice straw	24.17	Singha and Das (2012)
	Peat (Bruneian)	14.97	Zehra et al. (2015)

(II) ions, was less than 1, indicating that the metal ions were favourably adsorbed.

3.5. Adsorption mechanism

In order to propose a mechanism for the adsorption of nickel (II) and lead(II) ions onto natural peat, FT-IR analysis was performed (Fig. 9A) in addition to the measurement of the electrokinetic stability (Fig. 9B) of the sorbent before and after the adsorption process. Previously, other researchers (Li et al., 2007; Dahiya et al., 2008) using low-cost adsorbents for the removal of toxic metal ions have confirmed a mechanism based on ion exchange or on the formation of complexes with functional groups present on the adsorbent surface.

In the present work a mechanism is suggested (Fig. 10) based on ion exchange by the following functional groups: carboxyl (groups derived from a carbonyl group), phenolic, hydroxyl and ether, with positively charged ions of nickel(II) or lead(II). These groups are capable of bonding ions of

Table 5 Freundlich and Langmuir isotherms constants for nickel(II) and lead(II) ions adsorbed onto peat.

Adsorbed metal ion	Langmuir parameters			Freundlich parameters		
	R^2	q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n
Ni^{2+}	0.991	61.27	0.015	0.986	1.56	1.44
Pb^{2+}	0.992	82.31	0.449	0.525	18.72	1.86

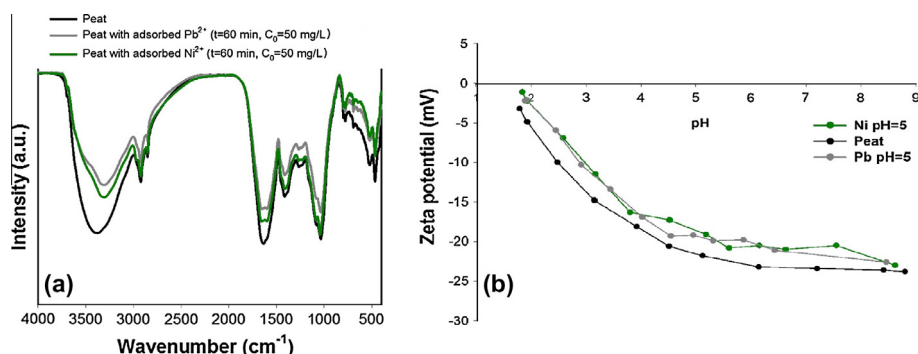


Figure 9 FT-IR spectra (a) and zeta potential curves (b) for nickel(II) and lead(II) ions adsorbed by peat (pH = 5).

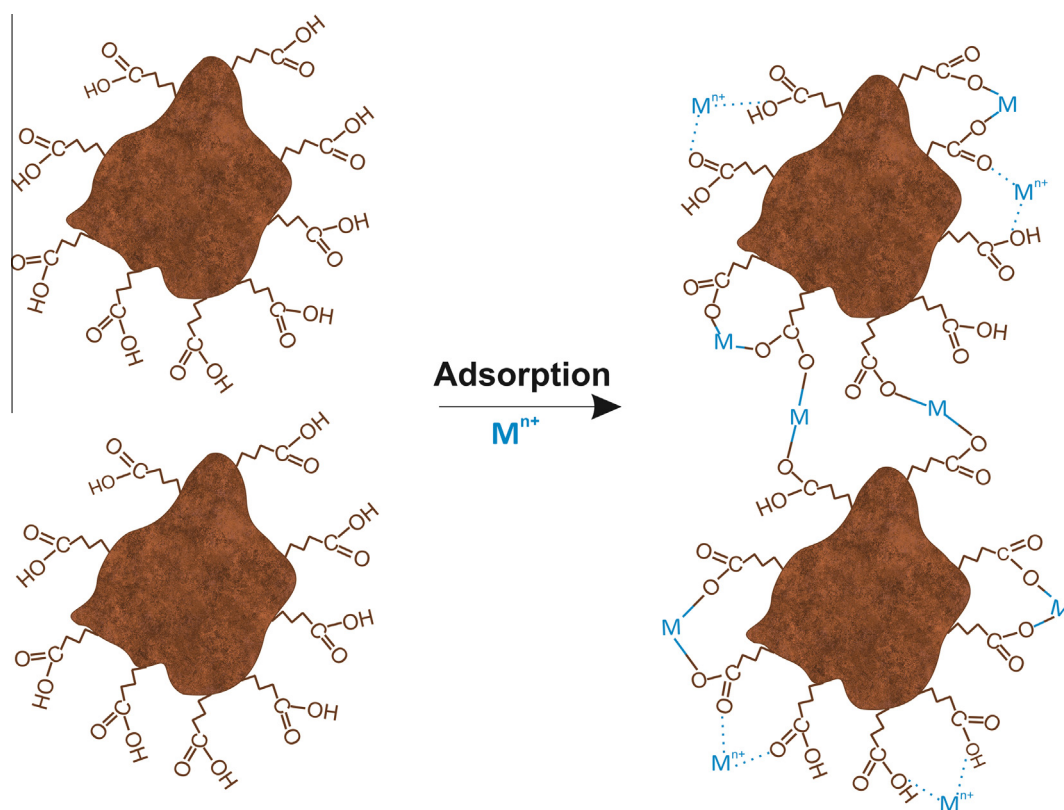


Figure 10 Example mechanism for the adsorption of nickel(II) and lead(II) ions on peat.

environmentally harmful metals through the dissociation of a hydrogen cation.

Analysis of the FT-IR spectra of the peat before and after adsorption (Fig. 9A) confirms the important role played by functional groups on the peat surface in the metal ion adsorption process. Based on the spectra obtained, it can be concluded that following the adsorption of either nickel(II) or lead(II) onto natural peat, the intensity of the relevant bands is reduced. This is particularly visible in the case of stretching vibrations of —OH groups in the range $3550\text{--}3300\text{ cm}^{-1}$ and stretching vibrations of C=O groups in the range $1680\text{--}1600\text{ cm}^{-1}$. After adsorption process lower intensity has also signal at 1413 cm^{-1} , associated with the stretching vibrations of C—OH groups in the structure of peat. The results show clearly that ions of the environmentally harmful metals form

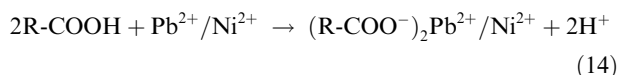
bonds with oxygen groups, at the same time causing separation of a hydrogen cation. Confirmation of this thesis are slightly shifts in the maximal wavenumbers of the signals characteristic for groups that are involved in creation of the interactions between hazardous metal ions and peat surface. These shifts are observed especially for the signal attributed to the —OH groups. Maximal wavenumber for this peak, in the spectrum of peat, is around 3420 cm^{-1} , and after adsorption of Ni^{2+} and Pb^{2+} ions is shifted to the 3385 cm^{-1} and 3394 cm^{-1} respectively. Similar observations are related to the signal attributed to the C=O groups. Before adsorption that signal has maximum at 1635 cm^{-1} and after the process maxima were shifted to the 1643 cm^{-1} for Ni^{2+} and to the 1641 cm^{-1} for Pb^{2+} ions. The spectra in Fig. 9A also show that the adsorption process is more effective for lead(II) than for nickel(II)

ions, as is indicated by the smaller intensity of particular bands obtained for peat with adsorbed Pb^{2+} ions. These results show excellent correlation with those obtained using atomic absorption spectrometry, which confirm that a greater effectiveness of adsorption on peat is obtained for lead(II) ions.

Fig. 9B shows the zeta potential curves for the peat samples with and without adsorbed Ni(II) and Pb(II) ions. A pH-dependent curve was plotted for the samples. For an aqueous suspension of peat the zeta potential value ranged from -5 mV for a pH of approximately 2, to -25 mV for a pH of 8. The zeta potential values suggest that the functional groups in the peat were highly deprotonated and negatively charged, indicating that the major binding sites are acidic groups.

At constant pH, the zeta potential value became more positive with an increase in either Pb^{2+} or Ni^{2+} concentration. This indicates that the ions' surface coordination is caused by the following:

- electrostatic attraction between the negative charge on the biomass and positive metal cations;
- and/or ionic exchange adsorption where Ni^{2+} and Pb^{2+} ions replace a proton from the surface adsorbent (substitution of protons in surface groups on metal ions), as outlined below:



As a consequence of this, a positive remaining charge could be located on the surface, making the zeta potential value more positive. The results of electrokinetic analysis and the FT-IR spectra confirm the correctness of the proposed mechanism of interaction between the analysed metal ions and peat.

The next confirmation of the mechanism based on the ion exchange principle is comparison of pH values of the solution before and after adsorption process (see Table 7). Experimental data collected confirm that increasing amount of metal ions adsorbed onto the adsorbent surface, the more hydrogen ions (H^+) get released out of peat into the water solution. Consequently, the pH value of the reaction mixture decreases. This effect is consistent with the ion exchange principles – the more ions were adsorbed on the peat, the more hydrogen ions were released into the solution, making the pH lower.

Table 7 Final pH values of the solution after adsorption metal ions (pH = 5 was the initial pH of the solution before adsorption).

Initial metal concentration (mg/L)	Final pH	
	Ni^{2+}	Pb^{2+}
15	3.98	3.90
30	3.81	3.69
50	3.57	3.41
100	3.28	3.15

Table 8 Desorption of nickel(II) or lead(II) ions from the spent peat using H_2O and HCl.

Initial metal ion concentration (mg/L)	Desorption percentage (%)					
	H_2O		HCl 0.05 M		HCl 0.1 M	
	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}
25	0.8	1.4	95.4	91.7	98.5	98.2
50	1.0	2.2	89.9	84.7	98.1	96.8
75	2.1	3.4	85.7	80.9	91.2	90.4
100	3.2	4.1	78.8	74.4	86.9	84.5

3.6. Desorption test

The possibility of reusing natural adsorbents multiple times increases the attractiveness of the adsorption process. An important element of the process is the development of an effective method for the regeneration of the materials used. For this purpose a desorption test was carried out, using water and hydrochloric acid in various concentrations (0.05 and 0.1 M) as the regenerating agent.

The results presented in Table 8 indicate that water is a weak desorbing agent. This is evidence of a strong bond between the adsorbate and adsorbent. Only when hydrochloric acid was used was a significant increase in the degree of desorption achieved. It was found that as the concentration of the hydrochloric acid used as a desorbing agent increased, there was an improvement in the effectiveness of the biosorbent regeneration process. The mechanism of desorption is based on the exchange of hydrogen ions (H^+) with the adsorbed metal ions. After regeneration, the sorbent could be used again in further adsorption tests.

4. Conclusion

The physicochemical characteristic of peat confirmed that it is very interesting material containing numerous of functional groups in its structure that can easily adsorb positively charged metal ions. The adsorption process studied is very complex and is determined by different parameters such as the concentration of model solution, contact time, mass of sorbent, and pH of the reaction system. During first 5 min the adsorption of analysed metal ions was very fast, and it reached equilibrium after maximum 60 min irrespective of model solution concentration. Slightly better results were obtained in the case of lead(II) ions whose adsorption efficiency reached 100% just after 3 min (15 and 30 mg/L), 5 min (50 mg/L) or 15 min (100 mg/L) of the process. It indicates the greater affinity of the peat surface for that metal ion. Moreover, it was noted that by increasing the contact surface between adsorbent and adsorbate solution, calculated by mass of the adsorbent, the efficiency of metal ions removal can be easily improved. Taking into account economic aspects and satisfactory results of adsorption the optimum mass of the adsorbent was set to 5 g/L. The most important factor determining the successful removal of nickel(II) and lead(II) ions onto peat was pH, which influence both adsorbent surface functional groups as well as metal ions form. To avoid precipitation of metal hydroxides and including the obtained results pH = 5 was

established as an ideal. The kinetics studies of the analysed process are relatively well described using the Lagergren pseudo-second-order equation, in particular type 1. This is confirmed by the high coefficient of correlation ($r^2 = 0.999$) obtained for all studied concentrations of model solutions. Additionally, it was proved that adsorption of nickel(II) and lead(II) ions onto peat has monolayer nature and experimental data obtained correspond to Langmuir isotherm model. Analysed natural adsorbent exhibits relative high sorption capacity, 61.27 mg(Ni²⁺)/g and 82.31 mg(Pb²⁺)/g, as compared to other materials studied so far. Potential regeneration of natural sorbent was confirmed with desorption test using hydrochloric acid.

All results considered, proved potential application of this type of natural sorbent in removal of nickel(II) and lead(II) ions from water solutions. Furthermore, the undoubted advantages of this material include its availability and low extraction costs, which may be of fundamental importance for its application in the purification of waste waters containing different types of metal ions.

Acknowledgement

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