Research article

Treatment of model solutions and wastewater containing selected hazardous metal ions using a chitin/lignin hybrid material as an effective sorbent

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ABSTRACT

A chitin/lignin material with defined physicochemical and morphological properties was used as an effective adsorbent of environmentally toxic metals from model systems. Particularly significant is its use in the neutralization of real industrial wastes. The ions Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} were adsorbed on the functional sorbent, confirming the high sorption capacity of the newly obtained product, primarily due to the presence on its surface of numerous active functional groups from the component biopolymers. The kinetics of the process of ion adsorption from model solution were investigated, and the experimental data were found to fit significantly better to a type 1 pseudo-second-order kinetic model, as confirmed by the high correlation coefficient of 0.999 for adsorption of both nickel(II) copper(II) zinc(II) and lead(II) ions. The experimental data obtained on the basis of adsorption isotherms corresponded to the Langmuir model. The sorption capacity of the chitin/lignin material was measured at 70.41 $mg(Ni^{2+})$/g, 75.70 $mg(Cu^{2+})$/g, 82.41 $mg(Zn^{2+})$/g and 91.74 $mg(Pb^{2+})$/g. Analysis of thermodynamic parameters confirmed the endothermic nature of the process. It was also shown that nitric acid is a very effective desorbing (regenerating) agent, enabling the chitin/lignin material to be reused as an effective sorbent of metal ions. The sorption abilities of the chitin/lignin system with respect to particular metal ions can be ordered in the sequence $Ni^{2+}<Cu^{2+}<Zn^{2+}<Pb^{2+}$. Tests were also performed with the adsorption of ions of nickel(II), copper(II), zinc(II) and lead(II) from wastewater obtained from galvanization and battery production plants, confirming the ability of the chitin/lignin sorbent to adsorb harmful ions from real industrial wastes.

1. Introduction

The widespread use of metals (including hazardous metals) in various branches of industry brings about serious environmental impacts and may have an adverse effect on all types of living organisms (Khoushab and Yamabhai, 2010). The subject literature describes numerous ways of treating water and industrial wastes containing environmentally harmful compounds (Raval et al., 2016a,b,c; Shah et al., 2016a; Shah et al., 2016b). These include biological methods (Kikuchi and Tanaka, 2012; Šmejkalová et al., 2003), procedures using filtration membranes (Barakat, 2011; Mungray et al., 2012; Landaburu-Aguirre et al., 2010), advanced oxidation processes (Bilinska et al., 2015; Błędzka et al., 2010; Skalska et al., 2010), extraction methods (Abdel-Aziz et al., 2013; Kakitani et al., 2006; Regel-Rosocka et al., 2015; Regel-Rosocka and Wiśniewski, 2011), electrochemical methods (Bazrafshan et al., 2015), ion exchange (Dąbrowski et al., 2004) and adsorption methods (Ciesielczyk et al., 2013; Kołodyńska, 2010; Raval et al., 2016a; Sprynskyy et al., 2006; Wysokowski et al., 2014; Rudnicki P. et al., 2014). These last have proven to be a cost-effective option, primarily in view of the low cost of processing and

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equipment, and the ease and small size of operations. Increasing use is being made of adsorbents of natural origin (Bartczak et al., 2015; Cho et al., 2005; El-Shafey, 2010; Senthil Kumar et al., 2011; Lalhruaitluanga et al., 2010; Lourie and Gjengedal, 2011; Šćiban et al., 2006; Wang et al., 2010; Wu et al., 2010; Zhao et al., 2012), including lignin (Betancur et al., 2009; Guo et al., 2008; Klapiszewski et al., 2015, 2017) and chitin (Saravanana et al., 2013; Schleuter et al., 2013).

The differentiated structure of lignin and the presence of diverse functional groups enable it to bind positively charged metal ions, including those harmful to the environment. The sorption capacity of lignin is dependent on its origin (Seifert, 2014; Todorciuc et al., 2009), the type of metal ions (Wan Ngah and Hanafiah, 2008) and the experimental conditions (Apostolopoulos et al., 2014; Delle Site, 2001). Unmodified lignin, obtained directly from black liquor as a waste product in the paper industry, demonstrates affinity to ions of certain environmentally harmful metals in the following order: Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II) (Guo et al., 2008). A similar study, considering the sorption capacity of unmodified lignin with respect to copper(II) ions, was carried out by Brdar et al. (2012). In turn, Liu et al. (2013a,b) used a modified form of lignin, confirming the ability of aminated-epoxy-lignin to adsorb ions of copper(II) and lead(II). It was found that the modified lignin has better capacity to bind Cu(II) than Pb(II) ions. A comparison of the effectiveness of adsorption of lead(II) and cadmium(II) ions was made by Demirbaş (2004), who showed that under similar process conditions, adsorption on modified lignin from beech and poplar wood was more effective for Pb(II) ions (8.2–9.0 mg/g) than for Cd(II) (6.7–7.5 mg/g). Another biopolymer, chitin, is also capable of removing environmentally harmful metal ions. It has a structure that enables the formation of complexes with metal ions, particular those of the transitional and neighboring groups. It is believed that a single ion may be bound by a single $-NH$ group, and by several $NHCOCH_3$ groups, which more effectively isolates the metal ion from neighboring ions (Mohan and Syed Shafi, 2013). Divakaran et al. (2012) investigated the adsorption on chitin of nickel(II) and chromium(VI) ions, confirming the effective binding of those ions to the biopolymer. In a study of the effectiveness of adsorption of environmentally harmful metal ions, Benguella and Benaissa (2002) carried out a series of optimizations of the process of adsorption of cadmium(II) ions on chitin, finding that the best fitting kinetic model was a pseudo-second-order model (with a correlation coefficient of $R^2 = 0.999$). Keleşoğlu (2007) compared the adsorption of ions of copper(II), lead(II), cadmium(II) and nickel(II) on chitin, and found the affinities of the biopolymer to those ions to be ordered in the sequence $Cu^{2+}>Pb^{2+}>Cd^{2+}>Ni^{2+}$. This has been confirmed by Gonzalez-Davila and Millero (1990) and by Trimukhe and Varma (2008).

Interest in studies of possible uses of lignin and chitin is currently growing, chiefly due to the availability and low cost of those biopolymers, as well as the fact that they are structurally interesting renewable materials (Benguella and Benaissa, 2002; Guo et al., 2008; Schleuter et al., 2013; Wysokowski et al., 2014). The interesting and unique physicochemical and structural properties exhibited by chitin/lignin systems motivated us to test such a material in the role of an effective biosorbent of ions of nickel(II), copper(II), zinc(II) and lead(II) from model aqueous solutions, as well as in the neutralization of real industrial wastes. The results were subjected to detailed analysis, including investigation of the kinetic, equilibrium and thermodynamic aspects of the adsorption process. In addition, preliminary desorption tests were carried out to investigate the possibility of multiple reuse of the biosorbent. Energy dispersive X-ray spectrometry and Fourier transform infrared spectroscopy analyses were also performed, and the porous structure of the material used in the adsorption tests was determined.

2. Experimental

2.1. Preparation of chitin/lignin sorbent

To obtain the chitin/lignin sorbent, an appropriate quantity of kraft lignin (reagent grade, Sigma-Aldrich, Germany) was first placed in a 15% solution of hydrogen peroxide (Chempur, Poland) to activate the functional groups on the surface of the lignin. The system was stirred for 30 min with a Eurostar Digital fast rotary mixer (IKA Werke GmbH & Co. KG, Germany) at approximately 1000 rpm. Next, α-chitin powder from crab shells (technical grade, Sigma-Aldrich, Germany) was added to the activated lignin solution, at a chitin/lignin mass ratio of 1:1. The system was stirred intensively for 2 h, and the resulting product was filtered under reduced pressure and washed several times with water to obtain a clear filtrate. It was then convection-dried in a Memmert dryer (Germany) at 105 °C for approximately 24 h. At the next stage, the resulting adsorbent underwent detailed physicochemical analysis. The prepared chitin/lignin sorbent was then subjected to thorough physicochemical analysis (see Supplementary Material, Table S1).

2.2. Batch adsorption experiments

The most significant part of the study concerned the adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions from model aqueous solutions. The precursors of the metal ions were inorganic salts: nickel nitrate(V) $Ni(NO_3)_2 \cdot 6H_2O$, copper nitrate(V) $Cu(NO_3)_2 \cdot 3H_2O$, zinc nitrate(V) $Zn(NO_3)_2 \cdot 7H_2O$, and lead nitrate(V) $Pb(NO_3)_2$ (all supplied by Avantor™, Poland). It was determined how the effectiveness of removal of the ions from aqueous solutions was affected by the process parameters: the contact time of adsorbent and adsorbate (1–180 min; $C_0 = 25, 50$ and 100 mg/L, pH = 5, m = 0.5 g, T = 25 °C), the pH of the aqueous system (1–9; $C_0 = 50$ mg/L, t = 60 min, m = 0.5 g, T = 25 °C), the mass of sorbent (0.1–2.0 g; $C_0 = 50$ mg/L, pH = 5, t = 60 min, T = 25 °C) and the temperature (25–40 °C; $C_0 = 50$ mg/L, pH = 5, t = 60 min, m = 0.5 g).

Model solutions containing metal ions were placed in conical flasks. Next an appropriate quantity of sorbent was added to the aqueous system, which was then mixed using an RO5 multiposition magnetic stirrer (IKA Werke GmbH & Co. KG, Germany). After the required time the resulting mixture was filtered under reduced pressure using suitable equipment and filters (Sartorius Stedim Biotech, Germany). The filtrate was analyzed using a Z-8200 atomic adsorption spectrometer (Hitachi, Japan) to determine the quantity of metal ions which had not been adsorbed on the chitin/lignin system.

To analyze the impact of pH on the effectiveness of the adsorption process, an appropriate quantity of HNO_3 (0.1–1 M) or NaOH (0.1–1 M) was added to the flasks containing the model solution so as to attain the required pH. The pH of the system was monitored using a CP-401 pH-meter (Elmetron, Poland). Subsequent stages of the process were carried out as described above.

The final process parameter to be analyzed was the temperature, which was controlled using an IKA KS 4000i incubator (Germany).

The final results obtained were applied to a wastewater system. Adsorption of Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} ions from solutions of this waste was carried out by a method analogous to that described previously, using the optimum parameters determined in the preliminary adsorption tests on model solutions of metal ions

(t = 60 min, pH = 5, mass of adsorbent = 0.5 g, ambient temperature) (Bartczak et al., 2015). The concentration of metal ions in the wastewater system used in the study was 3500 mg(Ni^{2+})/L, 3200 mg(Cu^{2+})/L, 3700 mg(Zn^{2+})/L, 3900 mg(Pb^{2+})/L. The industrial wastes containing nickel(II), copper(II) and zinc(II) ions were obtained from a galvanization plant, and those with lead(II) from a battery production plant. The wastes were diluted by a factor of 10 prior to the adsorption tests.

2.3. Data analysis

2.3.1. Kinetic study
The quantity of metal ions retained by the chitin/lignin sorbent at time t was calculated using the following equation:

$$q_t = \frac{(c_0 - c_t) \cdot V}{m} \tag{1}$$

where c_0 is the initial concentration of metal ions (mg/L), c_t is the concentration of metal ions after the adsorption process (mg/L), V is the volume of solution (L), and m is the mass of sorbent (g).

Kinetic adsorption data were modelled using both the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic equations as follows (Ho and McKay, 1999; Lagergren, 1898):

- pseudo-first-order (Lagergren equation):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \tag{2}$$

- pseudo-second-order (Ho and McKay equation):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where q_t is the quantity of metal ions adsorbed in a given time (mg/g), q_e is the quantity of metal ions adsorbed at equilibrium (mg/g), k_1 is the rate constant of the adsorption process for the pseudo-first-order model (1/min), and k_2 is the rate constant of the adsorption process for the pseudo-second-order model (g/mg min).

The equilibrium adsorption capacity (q_e) and adsorption rate constants (k_1 and k_2) were calculated using experimentally obtained plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t.

2.3.2. Equilibrium study
The quantity of metal ions retained by the chitin/lignin sorbent at equilibrium was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{4}$$

where q_e is the quantity of metal ions adsorbed at equilibrium (mg/g) and C_e is the equilibrium metal concentration (mg/L). Adsorption isotherms are commonly determined using the Langmuir (1918) and Freundlich (1906) models.

- Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{C_e}{q_m} \tag{5}$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the quantity of metal ions adsorbed per unit mass of adsorbent (mg/g), and q_m (mg/g) and b (L/mg) (L/g) are the Langmuir constants representing the maximum adsorption capacity.

- Freundlich:

$$\log q_e = \log KF + \frac{1}{n} \cdot \log Ce \tag{6}$$

where K_F (mg/g) and n are the Freundlich constants. If $n<1$ the adsorption is a chemical process, while if $n>1$ it is a physical process.

The adsorption parameters were calculated from the slopes and intercepts of the plots of C_e/q_e vs. C_e and $\log q_e$ vs. $\log C_e$ using linear regression.

An additional parameter of the Langmuir isotherm model is the coefficient of separation (R_L), which is calculated from equation (7):

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{7}$$

where C_0 is the initial concentration of metal ions and b is the Langmuir constant. A value of R_L equal to 0 indicates irreversible adsorption. A value higher than 0 but lower than 1 ($0 < R_L < 1$) indicates favorable adsorption, a value equal to 1 indicates linear adsorption ($R_L = 1$), and a value higher than 1 ($R_L > 1$) implies unfavorable adsorption.

Chi-square test (Ding et al., 2012) are commonly used to measure the goodness of fit. The Chi-square test can be defined by equation (8):

$$\lambda^2 = \sum_{i=1}^{m} \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,cal}} \tag{8}$$

where m is the number of experimental data.

2.3.3. Thermodynamic study
Thermodynamic parameters for the adsorption of metal ions on the chitin/lignin sorbent at different temperatures were calculated using equations (9–12):

$$K_c = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^o = -RT \ln K_c \tag{10}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{11}$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{12}$$

where ΔG^o (kJ/mol) is the change in the free energy of the system, ΔH^o (kJ/mol) is the change in the free enthalpy of the system, ΔS^o (kJ/mol·K) is the change in the free entropy of the system, R (8.314 J/mol·K) is the gas constant, K_c is the reaction equilibrium constant $(-)$, and T (K) is the temperature.

2.4. Desorption study

A very important factor in the utilization of adsorbents is the ability to regenerate the materials used. This is of fundamental importance in enabling the repeated use of sorbents to remove environmentally harmful metal ions from water systems, which also has economic consequences. For this reason, desorption tests were carried out, the desorbing agents used being water and nitric(V) acid in two concentrations (0.05 and 0.1 M). The method used to regenerate the chitin/lignin sorbent involved placing the desorbing agent (50 mL) in a flask and then adding an appropriate

quantity of used sorbent. The system was then mixed using an RO 5 magnetic stirrer (IKA Werke, Germany). After 60 min the mixture was filtered, and the filtrate was analyzed using atomic absorption spectrometry (AAS). The results were used to draw conclusions concerning the degree of regeneration of the sorbents.

2.5. Physicochemical characterization of chitin/lignin sorbent after the adsorption process

The effectiveness of the metal ion removal process was also determined indirectly using energy dispersive X-ray spectrometry and Fourier transform infrared spectroscopy (see Supplementary Materials, Fig. S1) analysis and by determining the porous structure parameters of the materials used in the adsorption tests.

Energy dispersive X-ray spectrometry analysis (EDS) of the selected materials was performed to further confirm the efficiency of the adsorption process of metal ions on the adsorbent. The EDS technique is based on an analysis of X-ray energy values using a semiconductor, with the use of a Princeton Gamma-Tech (USA) unit with a prism digital spectrometer. Before the analysis, the sample was fastened to the base with a carbon paste or tape. The presence of carbon materials is needed to create a conductive layer, which ensures the delivery of electric charge from the sample. Representative parts (500 μm^2) were analyzed for evaluation of the surface composition.

The parameters of porous structure were measured by means of low-temperature N_2 sorption using an ASAP 2020 instrument (Micromeritics Instrument Co., USA). Surface area was determined to an accuracy of ± 0.1 m^2/g, pore volume to ± 0.01 cm^3/g, and pore size to 0.01 nm. Porous structure parameters were determined both for the pure chitin/lignin sorbent used in the experiments, and for the products obtained following the adsorption tests.

3. Results and discussion

3.1. Parameters of the adsorption process

In the first stage of the study, it was determined how the time of contact between sorbent and adsorbate (with concentrations of nickel(II), copper(II), zinc(II) and lead(II) ions in the range 25—100 mg/L) affects the efficiency of metal ion adsorption. The experimental data obtained are shown in Fig. 1 A—C.

Adsorption was found to proceed extremely rapidly in the initial stage. In the first 15 min the adsorption efficiency exceeded 50% for each concentration of metal ions. Adsorption equilibrium was reached after 30 min when the initial ion concentration was 25 mg/ L, and after 60 min for the other concentrations. For a concentration of 50 mg/L the maximum adsorption efficiencies were 85.1, 85.5, 92.3 and 99.1% for ions of nickel(II), copper(II), zinc(II) and lead(II), respectively. Irrespective of the tested concentration, the chitin/ lignin system exhibits clearly the best affinity to lead(II), and the lowest to nickel(II) ions. In the case of all analyzed concentrations, no significant changes were recorded after the elapse of the optimum process time. A comparison may be made with the results of Liu et al. (2013a,b) concerning the removal of nickel(II), copper(II), zinc(II) and lead(II) ions using chitin in the form of a powder and nanofibrils (CNF) obtained by freeze-drying. For powder chitin it took 1500 min for adsorption equilibrium to be reached in the case of all of the analyzed ions, whereas using nanofibrils the time was reduced to approximately 500 min. With the use of lignin isolated from black liquor (a waste product of the paper industry) the highest adsorption efficiency was recorded for times of 60 min in the case of lead(II) and 80 min in the case of nickel(II), copper(II) and zinc(II) ions (Guo et al., 2008). The times taken to attain equilibrium when the analyzed biopolymers are used alone are
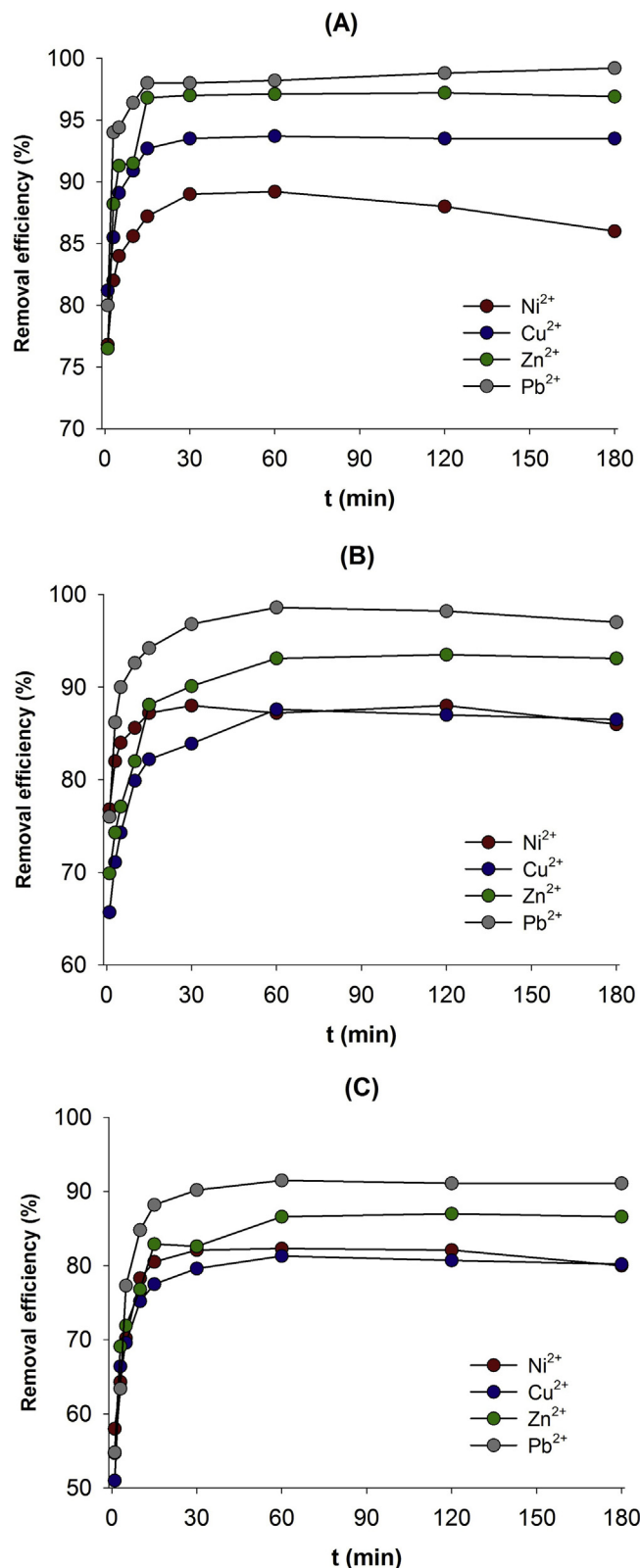

Fig. 1. Effect of contact time on the removal of nickel(II) copper(II), zinc(II) and lead(II) ions in concentrations of 25 mg/L (A), 50 mg/L (B) and 100 mg/L (C) by chitin/lignin biosorbent.

significantly longer than when the chitin/lignin system is used. Combination of these biopolymers enables a reduction in the process time for removal of metal ions from water systems.

A very important parameter in the process of adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions is the pH of the reaction system. This applies particularly to chitin/lignin material, a sorbent of natural origin whose surface contains numerous acid functional groups. The results in Fig. 2 A show that removal of metal ions is the lowest for pH = 1, because at low pH the concentration of H$^+$ is the highest and hydronium competes with the metal ions for access to the active sites of the adsorbent. At high pH the functional groups undergo dissociation and the surface of the adsorbent is negatively charged. This is of key importance in the case of positively charged metal ions. The optimum pH for all analyzed metal ions was found to be 5. A stepwise increase in pH causes dissociation of the acid functional groups of the adsorbent and reduction in the concentration of hydrogen ions in the solution, which in turn improves the access of metal ions to active sites on the adsorbent surface, increasing the effectiveness of the adsorption process. It is noted that over practically the entire pH range, the best removal is obtained for lead(II) ions.

Analogous results concerning the influence of pH on the effectiveness of removal of selected metal ions (copper(II) and lead(II)) have been obtained by other researchers, using adsorbents consisting of loofah fibers and keratin waste (Kong et al., 2014; Tang et al., 2014). When pure chitin (from Pelican Biotech) was used in the removal of copper(II) and lead(II) ions, maximum efficiency was obtained at pH > 6 (Karthik and Meenakshi, 2015; Kousalya et al., 2010). Guo et al. (2008) used lignin to adsorb nickel(II), copper(II), zinc(II) and lead(II) ions, again obtaining maximum effectiveness at pH greater than 6. Combining chitin and lignin allows the maximum effectiveness of metal ion removal to be attained at pH = 5 (more acidic). This is significant since industrial wastes are typically highly acidic (pH = 1—3), and it is often necessary to raise the pH of the system prior to the adsorption process to improve the effectiveness of decontamination.

The next parameter analyzed was the mass of sorbent (Fig. 2 B). It was found that when the quantity of sorbent was increased, the effectiveness of removal of metal ions from aqueous systems also increased. An increase in efficiency was observed up to the optimum dose of sorbent (5.0 g/L), for which optimum efficiency was attained. This is because an increase in the mass of sorbent causes an increase in the adsorptive (contact) surface and in the number of surface functional groups capable of removing metal ions, leading to higher effectiveness of the adsorption process.

The final parameter to be analyzed was the temperature of the system (Fig. 2 C). It was found that as the temperature increased there was a slight increase in the effectiveness of removal of all analyzed metal ions, which suggests an endothermic process. This question will be addressed in detail, with a comparison of the results with other published data, in section 3.4 — *Thermodynamic study*.

3.2. Adsorption kinetics

An important part of the study was the investigation of the kinetics of the process of adsorption of metal ions from model solutions with a concentration of 50 mg/L. Kinetic parameters for the adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions were determined using a pseudo-first-order model of Lagergren (1898) type and pseudo-second-order models of types 1—4 as described by Ho and McKay (1999). The parameters (see Table 1) were computed in the case of the pseudo-first-order model from a plot of $\log(q_e-q_t)$ against t (Fig. 3), and in the pseudo-second-order case from plots of t/q_t against t (type 1), $1/q_t$ against $1/t$ (type 2), $1/t$ against $1/q_t$ (type 3) and q_t/t against q_t (type 4).

The coefficients of correlation (r^2) obtained with the pseudo-first-order model for the adsorption of metal ions on the chitin/
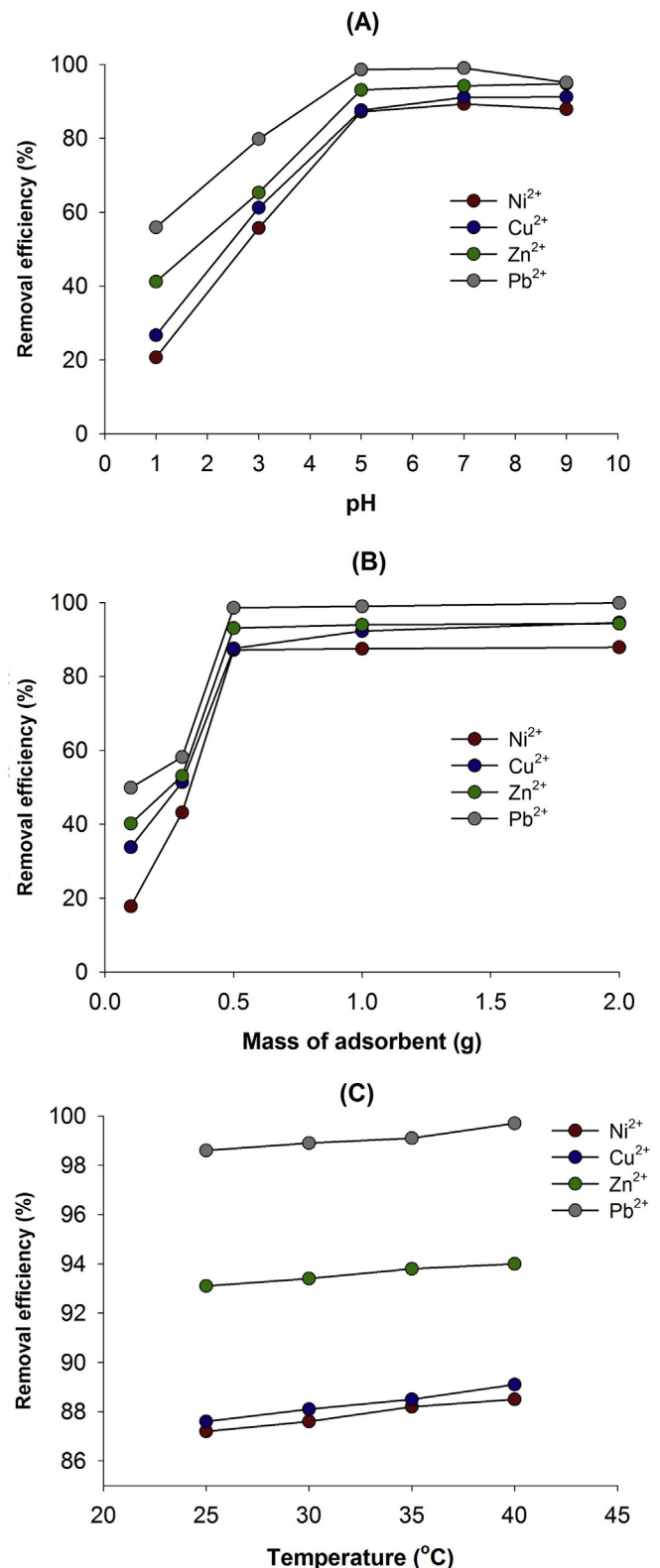

Fig. 2. Efficiency of adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions vs. tested process parameters.

lignin material lay in the range 0.854—0.983, which indicates only a moderately good fit of this model to the experimental data. This is confirmed by the large differences between the experimental quantities of adsorbed nickel(II), copper(II), zinc(II) and lead(II) ions

Table 1
Pseudo-first and pseudo-second order kinetic parameters for adsorption of metal ions on chitin/lignin material.

	Parameters		Metal ion type			
	symbol	unit	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
Kinetic model	$q_{e,exp}$	mg/g	8.80	8.76	9.35	9.86
Pseudo-first order	$q_{e,cal}$	mg/g	1.02	1.71	2.12	1.49
	k_1	min^{-1}	0.09	0.03	0.03	0.04
	r^2	–	0.983	0.854	0.930	0.900
Pseudo-second order type 1	$q_{e,cal}$	mg/g	8.66	8.71	9.38	9.76
	k_2	$g/mg^{-1}\,min^{-1}$	0.86	0.18	0.12	0.10
	h	$mg/g^{-1}\cdot min^{-1}$	34.45	13.68	10.71	9.76
	r^2	–	0.999	0.999	0.999	0.999
Pseudo-second order type 2	$q_{e,cal}$	mg/g	8.72	8.40	8.90	9.68
	k_2	$g/mg^{-1}\,min^{-1}$	0.81	0.37	0.35	0.36
	h	$mg/g^{-1}\cdot min^{-1}$	61.49	26.46	27.56	33.74
	r^2	–	0.944	0.832	0.745	0.964
Pseudo-second order type 3	$q_{e,cal}$	mg/g	8.73	8.51	9.09	9.70
	k_2	$g/mg^{-1}\,min^{-1}$	0.76	0.30	0.25	0.35
	h	$mg/g^{-1}\cdot min^{-1}$	58.04	22.02	20.54	32.53
	r^2	–	0.944	0.832	0.745	0.964
Pseudo-second order type 4	$q_{e,cal}$	mg/g	8.76	8.52	9.11	9.71
	k_2	$g/mg^{-1}\,min^{-1}$	0.73	0.29	0.24	0.33
	h	$mg/g^{-1}\cdot min^{-1}$	56.28	20.97	19.53	31.53
	r^2	–	0.947	0.793	0.698	0.948

($q_{e,exp}$) and the quantities of adsorbed ions computed from this kinetic model ($q_{e,cal}$).

A significantly better fit to the experimental data was obtained for the type 1 pseudo-second-order kinetic model. This is confirmed by the high values of the correlation coefficient (around 0.999) obtained for all analyzed metal ions, and by the good correspondence between the values of $q_{e,exp}$ and $q_{e,cal}$. The highest value of the reaction rate constant obtained using the pseudo-second-order model was 0.86 for nickel(II) ions.

The other types of pseudo-second-order model (2–4) were found to fit less well to the experimental data (Fig. 3). The values of the correlation coefficient (r^2) were lower than those obtained with the type 1 model (0.994–0.997 for nickel(II), 0.793–0.832 for copper(II), 0.698–0.745 for zinc(II) and 0.948–0.964 for lead(II) ions).

Use of the pseudo-second-order model (type 1) made it possible to obtain basic parameters relating to the kinetics of the adsorption process. Pseudo-second-order models are the type most commonly applied in investigating kinetic parameters, including in studies involving the use of chitin or lignin alone to remove metal ions from model aqueous solutions (see Table S2, Supplementary Materials).

3.3. Equilibrium study

Comparison of experimental data with different isotherm models is an important element of the design of an adsorption process. Fig. 4 shows the fit of the experimental data to particular models based on the plots of C_e/q_e against C_e and $\log(q_e)$ against $\log(C_e)$. In this way the isotherm parameters were computed (see Table 2).

Among the parameters of the Langmuir model, particularly noteworthy are the values obtained for the sorption ability (q_m) of the chitin/lignin system: 70.41 $mg(Ni^{2+})/g$, 75.70 $mg(Cu^{2+})/g$, 82.41 $mg(Zn^{2+})/g$ and 91.74 $mg(Pb^{2+})/g$. These indicate a significantly greater affinity to the surface of the adsorbent in the case of lead(II) ions, as has also been confirmed by other researchers using as adsorbents Na-clinoptilolite, ground shells of hazelnut and almond, and Ca(II)-imprinted chitosan microspheres (Bulut and Tez, 2007; He et al., 2014; Mihaly-Cozmuta et al., 2014). The

obtained dependences are related to the different degree of hydration of metal ions precursors ($Pb(NO_3)_2$, $Zn(NO_3)_2\cdot H_2O$, $Cu(NO_3)_2\cdot 2H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$). The higher degree of metal ion hydration, the more difficult the adsorption due to hindered access to the adsorbent surface and, consequently, the lower degree of its removal. Moreover, lead atom is bigger (180 pm) than other atoms (135 pm), which also influences its uptake from aqueous solutions. The electrons are easily polarised and retained by the nucleus to a lower degree (better match of the radius of metal ion, and also the symmetry of its electron orbital). The significantly greater sorption ability of the chitin/lignin system has already been noted in the sections on optimization of the process parameters and adsorption kinetics. Another basic parameter of the Langmuir isotherm model is the coefficient of separation (R_L), which for the adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions lay in the ranges 0.10–0.69, 0.07–0.55, 0.05–0.52 and 0.03–0.34, respectively. This indicates that the adsorption proceeded favorably. As regards the parameters of the Freundlich model (see Table 2), the value of the heterogeneity parameter (n) lay in the range 1.53–1.63 (n > 1) for the adsorption of nickel(II), copper(II), zinc(II) and lead(II). This indicates the physical nature of the interactions between adsorbate and adsorbent.

The correlation coefficients (r^2) were slightly higher for the Langmuir isotherm model, which suggests that the experimental data corresponded to that model. The small difference in the r^2 values suggests that adsorption of metal ions on the chitin/lignin material proceeds via a complex mechanism. The additionally conducted Chi-square test statistical analysis also confirmed the complexity of the adsorption process. If the values calculated from models are close to the experimental data, λ^2 will be a small number, which indicates a better fit. The obtained results (Langmuir model $\lambda^2 = 0.145$–7.864 and Freundlich model $\lambda^2 = 0.987$–8.128) did not allow to unambiguously establish which model is better for defining the adsorption of metal ions in the chitin-lignin system.

Table 3 shows a comparison of the maximum sorption capacities of various adsorbents with respect to nickel(II), copper(II), zinc(II) and lead(II) ions. In this study the chitin/lignin material demonstrated significantly better sorption capacity for lead(II) ions. This material may be used as an effective adsorbent of metal ions, and can certainly be competitive with other adsorbents. It exhibits significantly better sorption ability with respect to nickel(II), copper(II), zinc(II) and lead(II) ions than the biosorbents used separately. This confirms the sound basis for the present research, which has the aim of combining two waste materials – the material so obtained is found to have significantly better sorption properties with respect to metal ions.

3.4. Thermodynamic study

A further significant part of the work involved investigation of the thermodynamic aspects of metal ion adsorption on chitin/lignin biosorbent. Tests were carried out at four different temperatures: 25, 30, 35 and 40 °C. Changes in enthalpy and entropy were computed from the plot of $\ln K_c$ against $1/T$, using the gradient $\left(-\frac{\Delta H^o}{R}\right)$ and the intercept on the Y axis $\left(\frac{\Delta S^o}{R}\right)$. The results are given in Table 2.

The positive values of ΔH^o show the process to be endothermic, while the negative values of ΔG^o for adsorption at all four temperatures show it to be spontaneous. The changes in the entropy of the system (ΔS^o) describe the randomness in the interactions between adsorbent and adsorbate. Moreover the positive values of ΔS^o indicate the complex nature of the interactions. Similar results
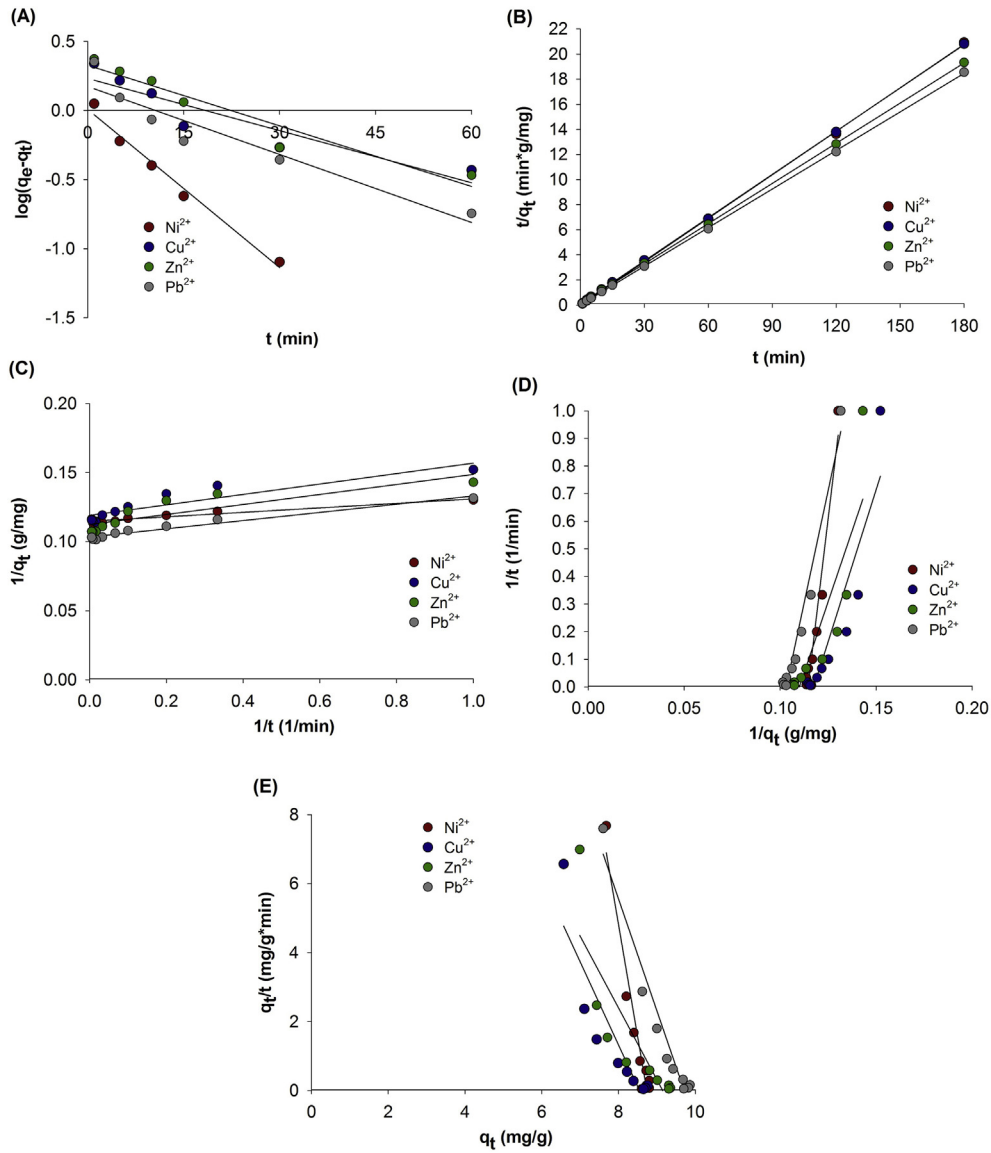
Fig. 3. Pseudo-first-order (A) and pseudo-second-order type 1 (B), 2 (C) 3 (D) and 4 (E) kinetic fit for adsorption of nickel(II), copper(II), zinc(II) and lead(II) on chitin/lignin material.
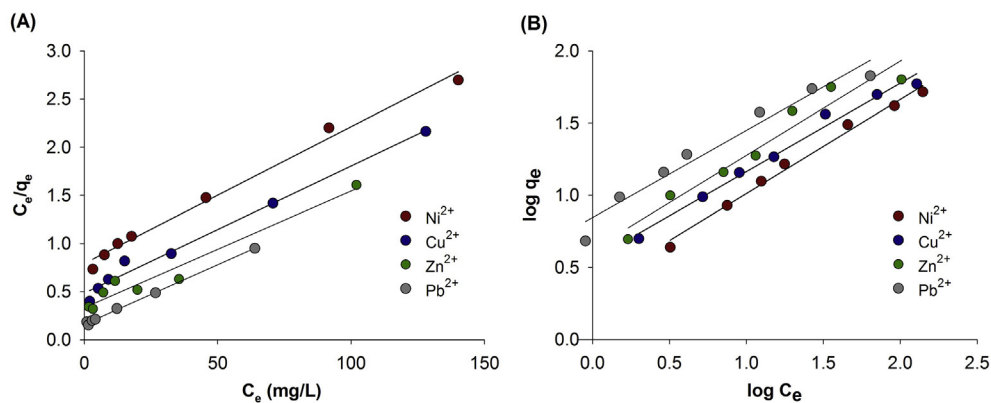
Fig. 4. Fit of experimental data for adsorption of metal ions to the Langmuir (A) and Freundlich (B) models.

were obtained by Bulut and Tez (2007) – irrespective of whether hazelnut or almond shells were used as the adsorbent, positive enthalpy values were obtained for all adsorbed metal ions: Ni^{2+} (32.49–47.29 kJ/mol), Cd^{2+} (12.21–17.76 kJ/mol) and Pb^{2+} (12.21–17.76 kJ/mol). These relationships were explained by the fact that positive values of ΔH^{o} suggest that adsorption is

Table 2
The value of parameters for the Langmuir and Freundlich isotherm models and thermodynamic parameters of the adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions onto chitin/lignin materials.

Parameters for the Langmuir and Freundlich isotherm models

Kind of adsorbed metal ion	Parameters of the Langmuir model				Parameters of the Freundlich model			
	q_m (mg/g)	b (L/mg)	R^2	λ^2	K_F (mg/g)	n	R^2	λ^2
i^{2+}	70.41	0.019	0.998	0.145	2.29	1.53	0.989	0.987
Cu^{2+}	75.70	0.027	0.986	1.189	3.56	1.63	0.985	1.196
Zn^{2+}	82.41	0.036	0.958	7.864	4.19	1.54	0.947	8.128
Pb^{2+}	91.74	0.069	0.995	0.189	6.83	1.59	0.970	2.500

Thermodynamic parameters

Type of metal ions	ΔH^o (kJ/mol)	ΔS^o (J/mol K)	ΔG^o (kJ/mol)			
			25 °C	30 °C	35 °C	40 °C
Ni^{2+}	7.07	24.53	−0.24	−0.37	−0.49	−0.61
Cu^{2+}	6.53	27.62	−1.70	−1.84	−1.98	−2.11
Zn^{2+}	8.73	35.07	−1.72	−1.90	−2.08	−2.25
Pb^{2+}	34.11	271.87	−46.90	−48.26	−49.62	−50.98

Table 3
Comparison of adsorption capacity of metal ions for different adsorbents.

Adsorbent	q_m (mg/g)	Adsorbed metal ions	Ref.
Chitin/lignin adsorbent	91.74	Pb^{2+}	This study
Lignin (black liquor)	89.51	Pb^{2+}	Guo et al., 2008
Chitin/lignin adsorbent	82.41	Zn^{2+}	This study
Chitin/lignin adsorbent	75.70	Cu^{2+}	This study
Chitin/lignin adsorbent	70.41	Ni^{2+}	This study
Bi-functionalized lignin	67.59	Pb^{2+}	Ge et al., 2014
Bi-functionalized lignin	48.53	Cu^{2+}	
Chitin micro-particles	42.62	Ni^{2+}	Liu et al., 2013a,b
Chitin micro-particles	38.36	Zn^{2+}	
Chitin micro-particles	23.45	Cu^{2+}	
Lignin (black liquor)	22.86	Cu^{2+}	Guo et al., 2008
Lignin (black liquor)	11.25	Zn^{2+}	
Modified chitin with polypyrrole	8.64	Pb^{2+}	Karthik and Meenakshi, 2015
Grafted chitin	6.40	Cu^{2+}	Kousalya et al., 2010
Lignin (black liquor)	5.99	Ni^{2+}	Guo et al., 2008
Chitin–humic acid	5.83	Ni^{2+}	Santosa et al., 2007
Carboxylated chitin	5.14	Cu^{2+}	Kousalya et al., 2010
Chitin (crab shells)	4.36	Ni^{2+}	Santosa et al., 2007
Protonated chitin	4.23	Cu^{2+}	Kousalya et al., 2010
Kraft lignin	3.37	Cu^{2+}	Šćiban et al., 2011
Kraft lignin	1.77	Zn^{2+}	Šćiban et al., 2011

endothermic, while negative values of ΔG^o indicate a spontaneous process. The increase in the effectiveness of ion removal at higher temperatures results from the expansion of the pores and activation of the surface of the adsorbent. Other researchers have analyzed the thermodynamics of Zn^{2+} ion adsorption using hazelnut shells (from the species *Corylus avellana* L.), again finding a positive enthalpy value (31.51 kJ/mol) which suggests an endothermic process of adsorption (Demirbaş and Karadağ, 2015).

3.5. Adsorption test using industrial wastewater

The final and an extremely important part of the research was a test of metal ion adsorption from wastewater systems. Following determination of optimal conditions for the adsorption process (t = 60 min, pH = 5, mass of adsorbent = 0.5 g, 20 °C) tests were carried out on wastewater obtained from battery production and industrial galvanization plants.

The obtained results show that, as in the case of adsorption of metal ions from model solutions, the highest process efficiency

(83%) is obtained for lead(II) ions. The affinities of the surface of the adsorbent to the analyzed ions are ordered in the following sequence: Ni^{2+} (70%) < Cu^{2+} (74%) < Zn^{2+} (77%) < Pb^{2+} (83%). The optimum conditions for the adsorption process determined using model aqueous solutions were transferred to a process of removal of pollutants from real systems, which is of fundamental importance for the potential use of the adsorbent in the purification of industrial wastes.

Similar tests of metal ion adsorption from real wastewater have been performed by other researchers. For example, Wan Ngah and Hanafiah (2008) and Cho et al. (2005) analyzed the treatment of wastewater from an electroplating plant using shells of crustaceans and mollusks as well as fly ash.

3.6. Desorption tests

The primary motivation for using adsorbents is the possibility of regeneration. In this study, desorption tests were carried out using as regenerating agents distilled water and nitric(V) acid at various concentrations (0.05, 0.1 and 0.5 M). The results appear in Table 4.

Regeneration tests were performed on biosorbents following a process of adsorption carried out under the following conditions: t = 60 min, pH = 5, m = 0.5 g. When water was used as the desorbing agent, a very low degree of elution was achieved for all of the analyzed metal ions (1.2–4.5%), indicating strong bonding between the adsorbate and adsorbent. When nitric(V) acid was used in the lowest concentration (0.05 M) moderate values were obtained for the desorption efficiency: 72.6, 75.6, 73.9 and 80.1% for ions of nickel(II), copper(II), zinc(II) and lead(II) respectively. Increasing the concentration of the inorganic acid to 0.1 M led to an improvement in the efficiency of elution of adsorbed metal ions, to 85.9, 87.7, 87.5 and 92.5%, respectively. The differences between the

Table 4
Desorption tests – regeneration sorbent.

Metal ion type	Desorption efficiency (%)			
	H_2O	HNO_3 0.05 M	HNO_3 0.1 M	HNO_3 0.5 M
Ni^{2+}	4.1	72.6	85.9	86.9
Cu^{2+}	4.5	75.6	87.7	88.5
Zn^{2+}	2.1	73.9	87.5	89.1
Pb^{2+}	1.2	80.1	92.5	94.1

Table 5
EDS analysis and porous structure properties of the used chitin/lignin hybrid material in the process of the nickel(II) and lead(II) ions adsorption ($C_0 = 50$ mg/L; time = 60 min; mass of adsorbent = 0.5 g; pH = 5).

Element	EDS analysis (% mas. contribution)			
	Material after adsorption of appropriate metal ions			
	Nickel(II)	Copper(II)	Zinc(II)	Lead(II)
Si	2.71	2.53	2.58	2.21
O	84.99	83.79	83.55	81.52
N	3.23	3.31	2.97	2.39
Ni	9.07	-	-	-
Cu	-	10.37	-	-
Zn	-	-	10.90	-
Pb	-	-	-	13.88

Porous structure properties				
Sample		BET surface area (m²/g)	Total volume of pores (cm³/g)	Mean size of pores (nm)
Chitin/lignin adsorbent		1.86	0.0330	37.76
Chitin/lignin material after adsorption process	Ni^{2+}	1.65	0.0079	30.82
	Cu^{2+}	1.52	0.0051	26.54
	Zn^{2+}	1.23	0.0045	32.43
	Pb^{2+}	1.04	0.0037	22.05

results obtained using acid in concentrations of 0.1 and 0.5 M were negligible. The literature contains significantly more reports in which hydrochloric acid is used as a desorbing agent, but nitric(V) acid was used in this study because it has the same anion as the salts used as precursors of the metal ions.

Other researchers have also used inorganic acids as eluting agents. Similar results were obtained in case of the regeneration of adsorbents obtained from the processing of banana skins. For the highest concentration of hydrochloric acid (0.1 M) the highest regeneration yield was obtained. When the acid concentration was lower (0.05 M) the results were not satisfactory. This is because, when the minimum acid concentration is increased, there is an increase in the quantity of H^+ ions available for exchange with the metal ions adsorbed by the acid functional groups on the adsorbent surface (Anirudhan et al., 2012). Other researchers used hydrochloric acid for elution of the adsorbed ions Cd^{2+}, Pb^{2+} (Coelho

et al., 2014) and Zn^{2+} (Kumar et al., 2012) from the surface of cashew shells. The results obtained with the eluting agent in a concentration of 0.1 M were 70.0, 87.9 and 63.9%. In tests of the desorption of Zn^{2+} ions from the cashew shell surface, the effect of the concentration of the eluting agent was also investigated. It was found that doubling the acid concentration brought only a small (4.3%) increase in the efficiency (Kumar et al., 2012).

The results show nitric(V) acid to be a very good desorbing agent, enabling the chitin/lignin material to be reused as an effective sorbent of environmentally harmful metal ions. This factor is of great importance for the development of economical and "green" technologies for purifying water systems.

3.7. Analysis of the adsorbent following the adsorption process

To obtain further confirmation of the effectiveness of adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions on the chitin/lignin adsorbent, the adsorbents used in the tests were subjected to energy dispersive X-ray spectrometry, porous structure analysis and FTIR spectral analysis (see Supplementary Materials, Fig. S1). Table 5 contains the results of EDS analysis of the adsorbents following adsorption of metal ions from model aqueous solutions (with selected metal ions at a concentration of 50 mg/L, pH = 5), giving the percentage contribution (by mass) of particular elements located on the adsorbent surface. The elements determined were silicon, oxygen and nitrogen, which occur in the structure of the adsorbent, and nickel, copper, zinc and lead, which were the elements adsorbed. The chitin/lignin material is built largely of carbon, which was not determined in this analysis, because the tested samples were placed on a carbon belt for good electrical conductivity.

The EDS analysis provides confirmation of the previous findings concerning the effectiveness of the adsorption process. The metal adsorbed from the model solution is found to be present on the surface of the adsorbent. This is indicated by the presence of characteristic bands, such as $Ni_{\alpha1}$, $Cu_{\alpha1}$, $Zn_{\alpha1}$, $Pb-M_{\alpha1}$ and $Pb-L_{\alpha1}$, on the EDS spectrum. The dispersive energies of these elements are 7.5, 8.0, 8.6, 2.3 and 10.6 keV, respectively. The examples EDS spectra were added to Supplementary materials – Fig. S3.
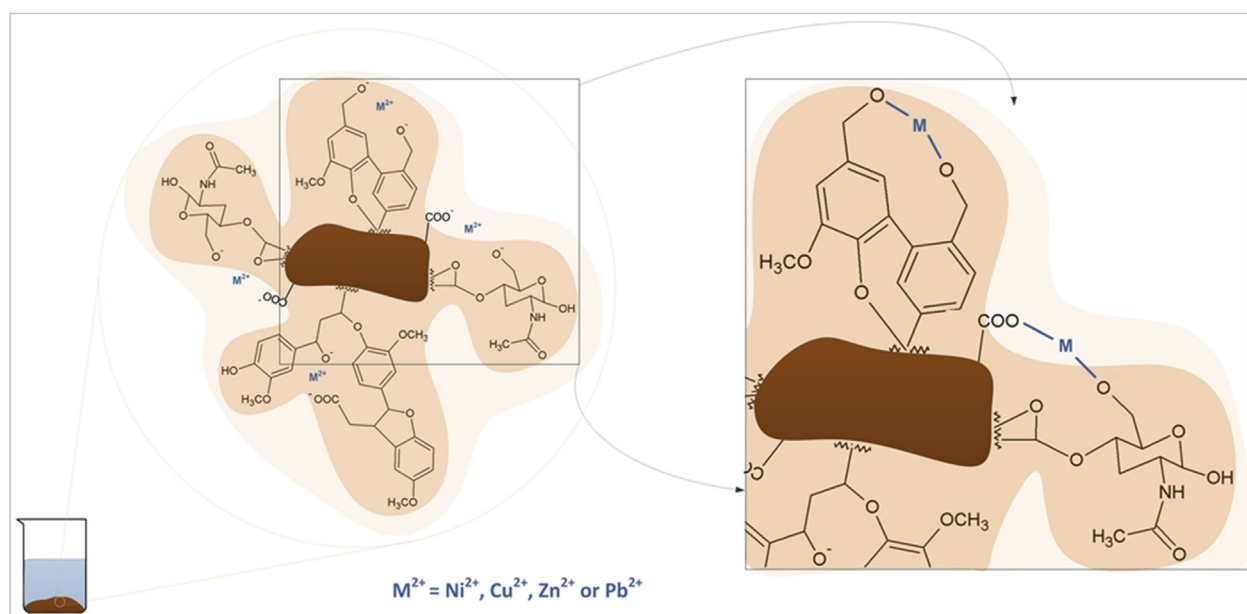
Fig. 5. Example mechanism for the adsorption of nickel(II), copper(II), zinc(II) and lead(II) ions on chitin/lignin material.

When metal ions were adsorbed from a solution of concentration 50 mg/L, the mass contributions of the respective metals on the surface of the hybrid adsorbent were as follows: 9.07% Ni(II), 10.37% Cu(II), 10.90% Zn(II) and 13.88% Pb(II). When the concentration of the model solution of adsorbate is increased, there is an increase in the quantity of metal found to be present in the structure of the adsorbent.

Energy dispersive X-ray spectrometry is a popular method for determining metals present on the surface of adsorbents. For example, EDS was used by Areco et al. (2013) to confirm the presence of Cu, Zn, Cd and Pb on the surface of *Avena fatua*.

The BET method was used to determine the porous structure parameters of the chitin/lignin material before and after the process of adsorption of metal ions from a solution of concentration 50 mg/L. The results are given in Table 5.

The specific surface area of the material used in the tests was found to decrease following the adsorption process, due to saturation of the active sites capable of capturing metal ions. The pore volume also decreased, again as a result of the filling of pores with the adsorbate.

Based on the analysis of kinetic, equilibrium and thermodynamic parameters, porous structure parameters, EDS and FTIR spectra, a mechanism can be proposed for the adsorption of metal ions on the chitin/lignin system. The suggested mechanism (Fig. 5) is based on ion exchange by the following functional groups: carboxyl (groups derived from a carbonyl group), phenolic, hydroxyl and ether, with positively charged metal ions. These groups are capable of bonding ions of environmentally harmful metals through the dissociation of a hydrogen cation. In addition, the pH of the system was measured before and after the adsorption process. It was found that the more metal ions are adsorbed on the adsorbent surface, the more hydrogen ions (H^+) are released from the chitin/lignin system into the aqueous solution. Consequently the pH of the reaction mixture decreased from 5 to the following values: 3.97 (Ni^{2+}), 3.90 (Cu^{2+}), 3.55 (Zn^{2+}) and 3.01 (Pb^{2+}). This effect is in accordance with the principles of ion exchange — the more ions are adsorbed on the chitin/lignin system, the more hydrogen ions are released into the solution, causing a drop in the pH.

4. Conclusions

The results presented in this paper show that chitin modified with lignin is a useful material for the removal of hazardous metals from model solutions as well as real industrial wastewaters. The chitin/lignin material obtained demonstrates good efficiency in removing nickel(II), copper(II), zinc(II) and lead(II) ions. The process of adsorption of selected metal ions can be described by a pseudo-second-order (type I) model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. These interactions were confirmed indirectly by means of FTIR spectroscopy. In the case of all of the selected divalent metal ions, the Langmuir model produced the highest linear correlation coefficient and better described the thermodynamic equilibrium for adsorption of the metals from model solutions. The chitin/lignin sorbent was found to have relatively high sorption capacities, equal to 70.41 mg(Ni^{2+})/g, 75.70 mg(Cu^{2+})/g, 82.41 mg(Zn^{2+})/g and 91.74 mg(Pb^{2+})/g. The highest affinity for the surface of the sorbent is found in the case of lead ions, which can be explained by the atomic structure: the lead atom has the largest atomic radius, valence radius and ionization potential (among the analyzed metal ions), which can have a significant impact on the efficiency of adsorption.

Preliminary tests performed on industrial wastewaters prove that chitin/lignin biosorbent may be used for the recovery of heavy metals from wastes originating from accumulator and battery production and from galvanization plants, especially for the removal of lead(II) ions.

Taking into account that the prepared sorbent is composed of chitin (a waste from the food industry) and lignin (a by-product of the pulp and paper industry), it is strongly believed that the unique properties of the obtained chitin/lignin material may point to a significant direction in the development of sustainable and environmentally friendly technologies.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.08.059.

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