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Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary

BATCH ADSORPTION OF Zn(II) IONS FROM AQUEOUS SOLUTION ONTO SAWDUST

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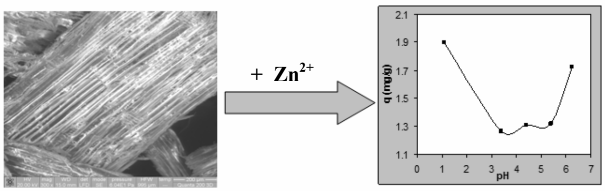
The removal of Zn(II) ion from aqueous solution by adsorption onto sawdust was examined in batch experiments. The sawdust used as adsorbent in this study is a waste obtained in large quantities in our country from wood processing industry. The experiments were performed in order to examined the influence of most important parameters (initial solution pH, adsorbent dose, initial Zn(II) concentration, contact time and temperature), and the obtained results were used to establish the optimum adsorption conditions. These were found to be an initial solution pH of 1.09 and 6.23, 8.0 g sawdust/L, 100 min of contact time and ambient temperature. The standard thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) were also evaluated and the obtained results have indicated that the adsorption process is thermodynamically favourable and endothermic.



INTRODUCTION

Numerous utilizations of zinc in industrial activities (such as: electroplating, metal processing, paint and pigment manufacture, etc.)[1] have seriously contributed to the contamination of water stream with this heavy metal in many regions of the world. Although, zinc is an essential element necessary for growth and metabolism of living organisms,[2] it may become toxic when its concentration exceeds the amount required for correct biological functioning.[3] Therefore, to ensure the quality of human life and also of environment, it is necessary the removal of Zn(II) ions from industrial effluents.

Currently, various methods such as chemical precipitation, ion-exchange, electrochemical treatment, reverse osmosis, membrane processes, etc,[4-6] are used for the removal of Zn(II) ions from industrial effluents. Unfortunately, such conventional treatment processes of industrial effluents have several important disadvantages related to high cost and energy consumption, low efficiency and selectivity. From this perspective, adsorption is considered as one of the most efficient and simple method that can be used for the removal of heavy

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metals, including Zn(II) ions, from aqueous effluents.[7, 8] All these advantages are related by the possibility of using various natural materials or agricultural and industrial by-products and wastes for the quantitative removal of numerous heavy metal ions by adsorption, including Zn(II) ions, in various experimental conditions.[9-11] Thus, adsorption shows great potential of commercial value in actual industrial wastewater treatment.

Sawdust is an inexpensive material which is available in large quantities in many regions where the wood processing is an important industrial activity. From chemical point of view, the sawdust is an organic material that contains mainly cellulose and lignin, in different proportions depending on the kind of wood from which it comes. Numerous studies from literature exhibited the ability of sawdust obtained from a given type of wood specie (pine, poplar, beech, etc.) to retain different heavy metal ions, including Zn(II), from aqueous solutions.[12-14] But, the sawdust resulted from industrial wood processing is a mixture from different wood species, and due to its diverse composition, this material is considered a waste and is mainly used as combustible for heating of production spaces. Unfortunately, the utilization of sawdust as combustible do not solve the problem of its discharge in environment, and in consequence the finding of new valorisation modalities, is an issue which is still worthy to study. Even if the composition of sawdust varies in relatively large limits as a function of raw wood specie, the nature of functional groups from its surface remain the same, and thus the utilization of this material as adsorbent for metal ions removal from aqueous solutions, can be a viable alternative for its valorization.

In this study, the removal of Zn(II) ions from aqueous solution using sawdust from wood processing industry as adsorbent was examined. The influence of most important experimental parameters, such as initial solution pH, adsorbent dose, initial Zn(II) concentration, contact time and temperature, on the efficiency of adsorption process has been studied in batch systems. The adsorption isotherm, kinetics and thermodynamic studies were conducted as well. Two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order kinetics models) were used for the modelling of experimental data. The adsorption mechanism was proposed according with the results obtained.

RESULTS AND DISCUSSION

Characterization of adsorbent material

The EDX spectrum (Fig. 1-inside) has shown that the sawdust contains in its structure relative high amounts of various chemical elements (as C, H, O, P, S. etc.) that can be included in different functional groups. Also, the presence of some mobile ions (ex. Na, K, Mg, Ca, Al) and its porous structure (see SEM image – Fig. 1-inside) are other arguments which recommend the utilization of this material for the removal of metal ions from aqueous solution.

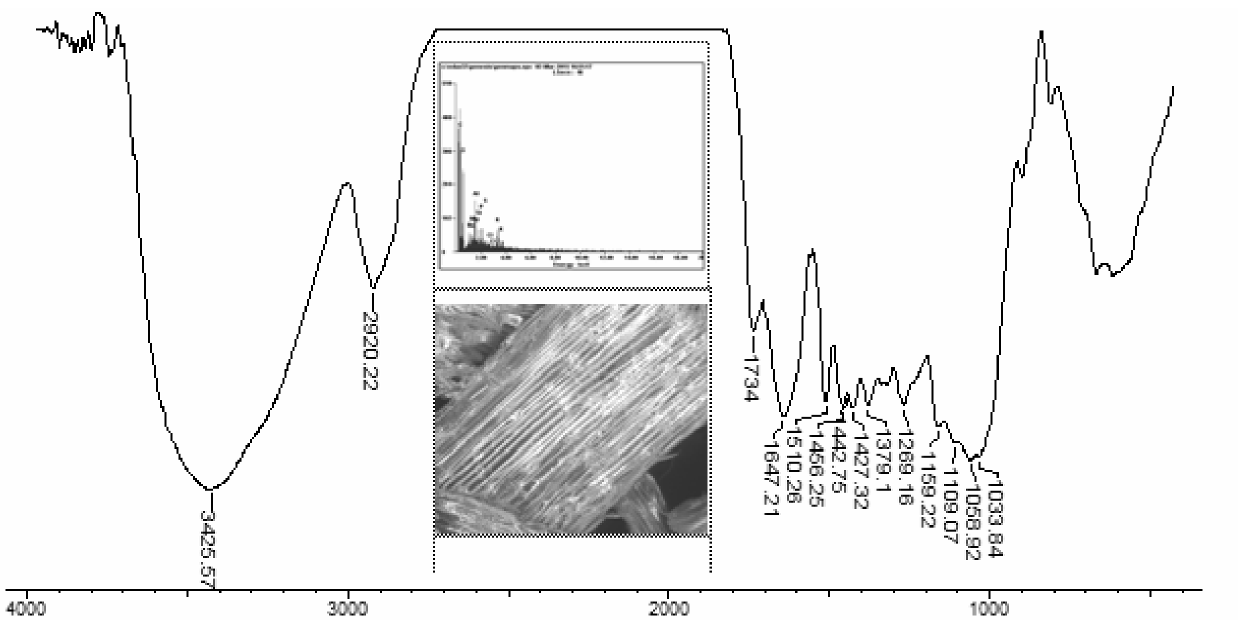

Fig. 1 – IR spectra, EDX spectra and SEM image of sawdust used as adsorbent.

The presence of various functional groups on the sawdust surface, which is potential binding sites for metal ions were highlighted by IR spectrum (Fig. 1). The most important functional groups are: aliphatic and aromatic hydroxyl groups (3425 and 1159 cm^{-1}), aliphatic radicals (2920 cm^{-1}), carboxyl groups (1734 cm^{-1}), carbonyl and ether groups (1647 cm^{-1}), aromatic radicals with branched structure (1510 – 1427 cm^{-1}), C–O groups from organic carboxylic compounds and their derivates or syringyl rings (1159 – 1033 cm^{-1}).[15, 16]

During the adsorption process these functional groups will interact with Zn(II) ions from aqueous solution, and consequently this material will act as a chemical substrate with cation exchange properties.

Influence of experimental parameters

Effect of initial solution pH

In this study, the initial pH of Zn(II) solution was varied between 1.09 and 6.23, at a constant Zn(II) concentration of 65.40 mg/L, contact time (24 h) and temperature (20 °C). This pH interval was chosen that the zinc to remains as free Zn^{2+} ions in solution. The obtained experimental results are illustrated in Fig. 2.

As can be observed from Fig. 2, the adsorption of Zn(II) ions onto sawdust depends by the pH of initial solution, but the variation of adsorption process efficiency is atypical one. The experimental results have shown that significant values of amount of Zn(II) retained on mass unit of sawdust are obtained both at pH of 1.09 (q = 1.89 mg/g) and at pH of 6.23 (q = 1.73 mg/g), which suggest the presence of two types of interactions in the adsorption mechanism of Zn(II) on this material.

Thus, at pH of 6.23, the adsorption process of Zn(II) ions is mainly determined by the presence of dissociated functional groups from sawdust surface that favour the electrostatic interaction of ion exchange type between metal ions positively charged and negatively charged functional groups. The reach of adsorption maximum in weak acid-neutral media (pH = 4.0 – 6.5) is a frequent behaviour and was reported in literature for the most low-cost materials used for Zn(II) removal.[10, 11]

In strong acid media (pH = 1.09), the high efficiency of adsorption process may be due to: (i) the electrostatic interactions, and in this case zinc must be in solution as a negative complex (ZnX_4^{2-}), which can interact with protonated functional groups on the surface of adsorbent; or (ii) the retention of Zn(II) ions is carried out by hydrogen bonds that are formed between hydrated metal ions and protonated hydroxyl groups on the sawdust surface.

In order to check the first hypothesis, additional experiments were performed where 0.1 mol/L HNO_3 solution used to obtain the pH value of 1.09, was replaced by HCl (0.1 mol/L). Under these conditions, in aqueous solution metal ions are predominantly as $ZnCl_4^{2-}$ complex, and the two negative charges can be involved in electrostatic interactions with protonated functional groups. The obtained results show that the adsorption of the anionic complex of zinc is lower than in case of hydrate Zn(II) ions, and therefore we can say that this type of interactions is not important in the removal process under these conditions. The most probable, the high efficiency of Zn(II) adsorption process in strong acid media (pH = 1.09) is due to the formation of hydrogen bonds between the water molecules that hydrated the Zn(II) ions and protonated hydroxyl groups of the adsorbent. Therefore, both initial solution pHs of 1.09 and 6.23 were considered as optimum values, and were used in all further experiments.

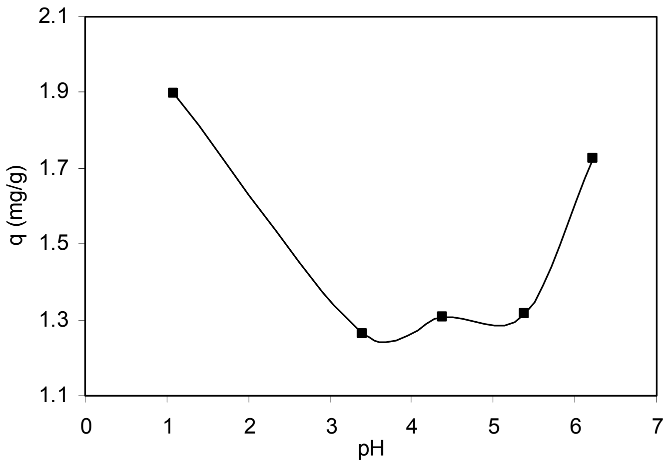

Fig. 2 – Effect of initial solution pH on the adsorption of Zn(II) ions onto sawdust.

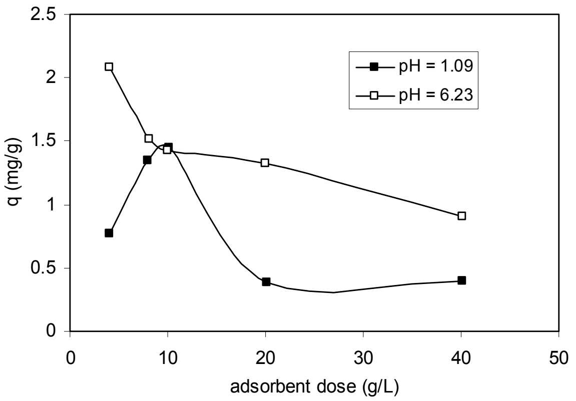

Fig. 3 – Effect of adsorbent dose on the Zn(II) adsorption onto sawdust.

Effect of adsorbent dose

The adsorbent dose is an important experimental parameter influencing both the operation cost and efficiency of adsorption process. In this study, the adsorbent dose was varied from 4.0 to 40.0 g/L, at a constant initial Zn(II) concentration of 65.40 mg/L, contact time (24 h) and temperature (20°C), for both pH values considered optimal. The obtained results are presented in Fig. 3.

It can be observed that the increase of adsorbent dose from 4.0 to 40.0 g/L determined the decrease of the amount of Zn(II) retained on mass unit of adsorbent from 2.08 to 0.89 mg/g when the initial solution pH is 6.23, while in strong acid media (pH = 1.09) the values of q rise with increasing of adsorbent dose in the range 4–10 g sawdust/L, after that decrease.

As expected, at initial solution pH 6.23 the increase of adsorbent dose over this range determined the decrease of adsorption capacity of the adsorbent. In case of initial solution pH 1.09, the increase of adsorption capacity at lower values of adsorbent dose is probably due to the agglomeration phenomena of adsorbent particles, which become insignificant with the increase of adsorbent dose. Therefore, an adsorbent dose of 8.0 g/L was considered as optimal for the Zn(II) removal from aqueous solution by adsorption onto sawdust, and was used in all further experiments.

Effect of Zn(II) initial concentration and temperature

The adsorption capacity of sawdust as a function of initial Zn(II) concentration was studied in a concentration range between 5.23 and 78.48 mg/L, at three different temperatures (10, 20 and 55.5°C), under optimal experimental conditions (initial solution pH of 1.09 and 6.23; adsorbent dose of 8.0 g/L; contact time of 3 h). The obtained results (Fig. 4) have shown that the adsorption capacity of sawdust increase with the increasing of Zn(II) concentration from aqueous solution for all studied temperatures, and this is more evident in case of adsorption systems with pH of 6.23.

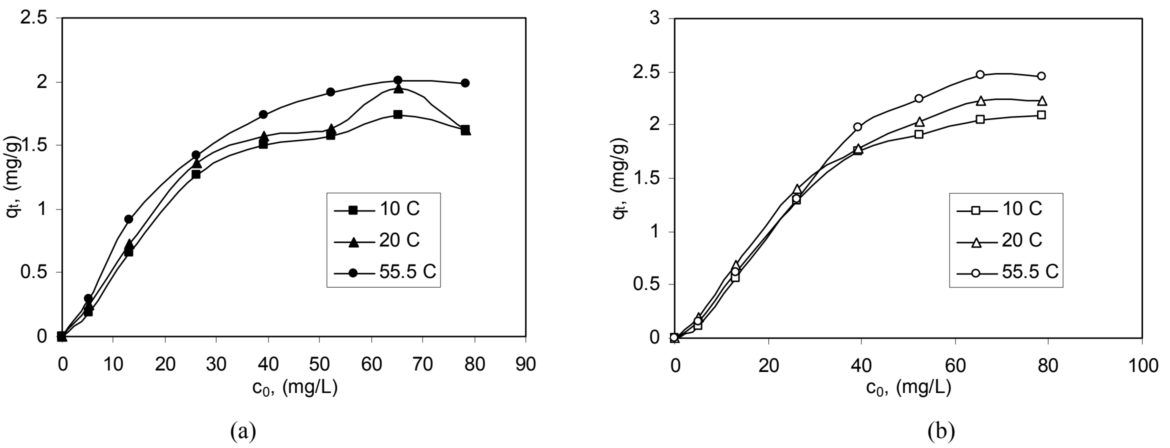

Fig. 4 – Effect of initial Zn(II) ions concentration on the adsorption onto sawdust at initial solution pH of 1.09 (a) and 6.23 (b), respectively.

Thus, when the initial Zn(II) concentration increase from 5.23 to 78.48 mg/L at 20°C, the adsorption capacity of sawdust increase from 0.44 to 1.13 mg/g at initial solution pH of 1.09 (Fig. 4a) and from 0.35 to 1.64 mg/g at initial solution pH of 6.23 (Fig. 4b), respectively. This variation is mainly determined by the fact that higher Zn(II) concentrations not only provide a larger driving force to overcome all mass resistances between the aqueous and solid phases, but also determined a higher probability of collision between metal ions and adsorbent surface.[17]

It should be also noted that the adsorption capacity of sawdust is increased by the increasing of temperature (Fig. 4). The experimental results indicate that for an initial Zn(II) concentration of 78.48 mg/L, the rise of temperature from 10 to 55.5°C determined the increase of adsorption capacity from 1.62 to 1.98 mg/g, and from 2.08 to 2.45 mg/g in case of adsorption systems with initial solution pH of 1.09 and 6.23, respectively. This variation it is an indication about the endothermic nature of adsorption process.

However, these values suggest that for the removal of Zn(II) ions by adsorption onto sawdust it is not necessary the increase of temperature, because the cost related to the obtaining of high temperatures is not covered by increasing of adsorption efficiency. In consequence, the Zn(II) adsorption onto sawdust can be carried out at ambient temperature and this is more advantageous from the economic point of view.

Adsorption isotherms

The adsorption capacity of a given material can be predicted by using its equilibrium adsorption isotherms, which are characterized by certain parameters that can offer useful information related to the adsorption process. In this study, the equilibrium isotherms have been modelled using the Langmuir and Freundlich isotherm models.

Langmuir model consider that the adsorption occurs until complete monolayer coverage is formed at the surface of adsorbent.[18] This model is useful in the estimation of maximum adsorption capacity (q_{max}, mg/g) that correspond to the surface saturation, and can be written in its linear form as:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{c_e}{q_{\max}} \qquad (1)$$

where: q_e is the amount of Zn(II) ions adsorbed on mass unit of sawdust at equilibrium (mg/g), q_{max} is the maximum adsorption capacity, corresponding to complete monolayer coverage on the surface (mg/g) and K_L is the Langmuir constant (L/mg).

The Langmuir model parameters (q_{max} and K_L) are calculated from the slopes and intercepts of the linear c/q_e vs. c plots.

Freundlich model describe the adsorption on heterogeneous surface or surface supporting different binding sites and is not restricted to the formation of a monolayer.[19] This model is useful in estimation of adsorption intensity, and its linear form is given by the equation:

$$\lg q_e = \lg K_F + \frac{1}{n} \lg c_e \qquad (2)$$

where: K_F is Freundlich constant and $1/n$ is the heterogeneity factor (the closer the *1/n* value is to zero, the more heterogeneous is the surface).

Both parameters of Freundlich isotherm model are obtained from the slopes and intercepts of the linear dependences lg q_e vs. lg c_e.

For each isotherm model, the characteristic parameters were calculated from its linear form, and the obtained values are presented in Table 1.

Table 1

Isotherm parameters for the adsorption of Zn(II) ions from aqueous solution onto sawdust

Langmuir model						
t(°C)	pH = 1.09			pH = 6.23		
	R^2	q_{max}(mg/g)	K_L(L/mg)	R^2	q_{max}(mg/g)	K_L(L/mg)
10	0.9551	2.4564	0.0496	0.9380	6.0643	0.0131
20	0.9432	2.3798	0.0651	0.9689	7.2046	0.0157
55.5	0.9974	2.3202	0.1131	0.9664	9.6712	0.0187
Freundlich model						
t(°C)	pH = 1.09			pH = 6.23		
	R^2	1/n	K_F	R^2	1/n	K_F
10	0.8374	0.7174	0.3887	0.8425	1.0410	0.2560
20	0.8498	0.6118	0.4724	0.8956	0.8165	0.3776
55.5	0.8570	0.5607	0.5446	0.9044	1.0015	0.2964

Table 2

Comparative values of Langmuir adsorption capacities for Zn(II) ions of some low-cost materials

Adsorbent material	pH	q_{max}(mg/g)	Reference
Palm leaves	5.50	14.60	13
Corn husks	7.50	6.80	15
Rice bran	5.00	13.10	14
Poplar sawdust	6.00	5.10	16
Fir sawdust	6.00	6.11	16
Sawdust	1.09	2.38	this study
	6.23	7.20	this study

Comparing the values of coefficients of determination (R^2) obtained for each model for each studied value of temperature, both at pH 1.09 and 6.23, it can be said that the adsorption process of Zn(II) onto sawdust is most accurately described by the Langmuir model. Therefore, the surface of sawdust can be considered to be homogeneous, and the adsorption of Zn(II) is carried out until a formation of a monolayer which covers the surface of adsorbent particles. The maximum adsorption capacity (q_{max}, mg/g) calculated from Langmuir model, increases with increasing of temperature at pH 6.23, while at pH 1.09 the variation is inverse. Also, the values of this parameter are higher at pH 6.23 than at pH 1.09, but are comparable with the Langmuir capacities of other materials tested in literature as low-cost adsorbents for Zn(II) ions removal (Table 2), which suggests the potential applications of this material in the industrial processes of wastewater treatment. On the other hand, the Langmuir constant (K_L, L/mg), which is a constant related to the energy of adsorption process, increase with the increasing of temperature, both for pH 1.09 and 6.23, respectively. These observations sustain the above hypothesis according to which the adsorption of Zn(II) from aqueous solution occurs through different type of interactions depending on the initial solution pH.

In case of Freundlich model, the values of coefficients of determination (R^2) are lower than in case of Langmuir model (Table 1), which indicate that this model is not so adequate to describe the adsorption process of Zn(II) ions onto sawdust.

Effect of contact time and adsorption kinetics

In Fig. 5 is presented the effect of contact time on the Zn(II) ions removal efficiency by adsorption onto sawdust, at constant initial metal ions concentration (26.15 mg/L), temperature (20 °C) and both values of initial solution pH (1.09 and 6.23).

It can be seen that the amount of Zn(II) adsorbed onto sawdust increases sharply in the first 30 min, and reach the equilibrium after 60 min. The Zn(II) adsorption rate is fast in the first stage, mainly due to the high number of available functional groups and high gradient of Zn(II) concentration. As the process takes place, the adsorption rate is reduced and become constant after 60 min. To be sure that the equilibrium of biosorption process is establish, a contact time of 3 hours was considered as sufficient and was used in all subsequent experiments.

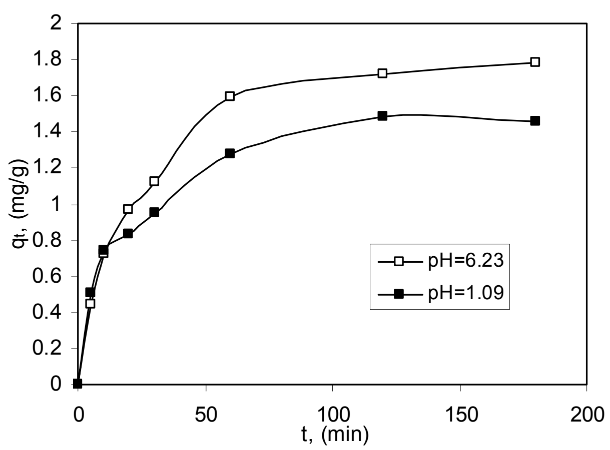

Fig. 5 – Effect of contact time for Zn(II) adsorption onto sawdust.

Table 3

Kinetic parameters for the adsorption of Zn(II) ions from aqueous solution onto sawdust

Pseudo-first order kinetic model				
pH	q_e^{exp}(mg/g)	R^2	q_e^{calc}(mg/g)	k_1(1/min)
1.09	1.48	0.9826	1.08	0.0117
6.23	1.78	0.9958	1.59	0.0428
Pseudo-second order kinetic model				
pH	q_e^{exp}(mg/g)	R^2	q_e^{calc}(mg/g)	k_2(g/mg min)
1.09	1.48	0.9958	1.59	0.0428
6.23	1.78	0.9983	1.97	0.0271

The obtained results were fitted using two kinetic models (pseudo-first order and pseudo-second order models), in order to test the mechanism that controlled the adsorption process of Zn(II) onto sawdust, in mentioned experimental conditions. The mathematical equations of these two kinetics models, in their linear forms are:[20, 21]

$$\lg(q_e - q_t) = \lg q_e - k_1 \cdot t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{t}{q_e} \qquad (4)$$

where: q_e and q_t are the amounts of Zn(II) retained on mass unit of sawdust at equilibrium and at time t (mg/g), k_1 is the rate constant of pseudo-first order kinetic model (1/min) and k_2 is the pseudo-second order rate constant (g/mg min).

The kinetic parameters of adsorption process of Zn(II) onto sawdust corresponding to pseudo-first order and pseudo-second order kinetics models were determined from the slopes and intercepts of linear dependences lg (q_e-q_t) vs t and t/q_t vs. t, respectively, and the obtained values are summarized in Table 3.

It can be seen that pseudo-first order kinetic model has a limited applicability for describing the kinetics of Zn(II) adsorption onto sawdust. Moreover, the equilibrium adsorption capacity values calculated in pseudo-first order kinetic equation (q_e^{calc}, mg/g) are very different from the experimental values obtained (q_e^{exp}, mg/g), in the experimental conditions considered optimal (see Table 3). In case of pseudo-second kinetic model, the very good correspondence between calculated and experimental values of q_e (Table 3) suggest that the adsorption of Zn(II) ions onto sawdust comply with this kinetic model. Therefore, the rate limiting step of the adsorption process involve chemical interactions between two partners: metal ions from aqueous solution and functional groups from adsorbent surface, and such behaviour has been reported in literature for different adsorbent materials.[10, 21]

Thermodynamics of adsorption

In order to characterize the thermodynamic behaviour of adsorption process of Zn(II) ions onto sawdust, the following standard thermodynamic parameters were used: free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0), whose values have been calculated using Langmuir constant (K_L) obtained at the three values of temperature, and van't Hoff equations,[22, 23] and the values of thermodynamic parameters obtained form each case are shown in Table 4.

Table 4

Thermodynamic parameters for Zn(II) ions adsorption onto sawdust

pH	t(°C)	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0(J/mol K)
	10	-15.88		104.25
1.09	20	-16.90	13.64	104.18
	55.5	-19.42		100.60
	10	-19.03		115.38
6.23	20	-20.36	15.66	116.00
	55.5	-24.34		115.56

The negative values of the standard free energy change (ΔG^0) obtained for all studied temperatures at both values of initial solution pH indicate that the adsorption process of Zn(II) ions onto sawdust is thermodynamically favorable. In addition, because the values of ΔG^0 are in the range of -15 ÷ -30 kJ/mol, suggests that in the adsorption mechanism predominant are electrostatic interactions (ion exchange or hydrogen bonds), and less those covalent or coordination.[22] Also, the values of enthalpy change (ΔH^0) confirms the experimental results obtained in the study of temperature effect, and shows that the adsorption of Zn(II) ions onto sawdust is an endothermic process for both initial solution pHs. Both the endothermic effect and positive values of entropy change could be explained if the change in Zn(II) hydration is taken into account. In solution Zn(II) is strongly hydrated while in the adsorbed state it loses a part of its hydration sphere, the process being strongly endothermic and with an increase in entropy due to water molecules liberation.

EXPERIMENTAL

Materials

The sawdust used in this study as adsorbent is a mixture of various coniferous wood species and was obtained from a local wood processing company (Romania), where is considered a waste. The sawdust samples were washed several times with distilled water to remove impurities, was dried in an oven in air for 6 hours at 75-80 °C, mortared and then stored in desiccators for subsequent use. The surface morphology of sawdust was analyzed by scanning electron microscopy (SEM-Hitachi S 3000 N) coupled with energy dispersive X-ray spectrometer (Bruker EDX Spectrometer). IR spectrum was recorded by the KBr pellet method on Bio-Rad IR Spectrometer, in the region between 400 and 4000 cm^{-1}, with a 4 cm^{-1} resolution. All chemical reagents used in this study were of analytical grade and were used without supplementary purifications. Stock solution of Zn(II) (10^{-2} mol Zn(II)/L) was prepared by dissolving an appropriate amount of zinc nitrate in distilled water. Working solutions were prepared by diluting the stock solution with distilled water. Distilled water, obtained from a commercial distillation system, was used for the preparation and dilution of working solutions.

Experimental procedure

All the adsorption experiments were performed at room temperature (20 ± 0.5 °C). The mixture containing a given amount of sawdust and 25 mL of 65.40 mg/L of Zn(II) solution was intermittent stirred for 24 h. After the adsorption procedure was finished, the solid and liquid phases were separated by filtration and Zn(II) concentration in solution was spectrophotometrically analyzed (Digital Spectrophotometer S 104 D) with xylenol orange (λ = 570 nm, 1 cm glass cell, against distilled water) using a prepared calibration curve. The effect of pH on adsorption was performed on the Zn(II) solutions with different pH values ranging between 1.09 and 6.23 (adjusted with 0.1 mol/L HNO_3 or NaOH solutions). The influence of adsorbent dosage on the adsorption was carried out by adding various amount of sawdust (4 – 40 g/L) in Zn(II) solution. The adsorption capacity (q, mg/g) and removal efficiency (R, %) were calculated from experimental data according to the following equations:

$$q = \frac{(c_0 - c)\cdot V}{m} \quad (5)$$

$$R = \frac{c_0 - c}{c_0}\cdot 100 \quad (6)$$

where: c_0 is the initial concentration of Zn(II) solution (mg/L), c is the residual concentration of Zn(II) solution (mg/L), V is volume of solution (mL), and m is the biosorbent mass (g).

In the interpretation of experimental results have been used the following notations: q and c – the adsorption capacity and residual Zn(II) concentration, after 24 hours of contact time, q_e and c_e – the adsorption capacity and residual Zn(II) concentration, at equilibrium, and q_t and c_t – the adsorption capacity and residual Zn(II) concentration, at time t.

The optimal conditions established in this way were used for the further experiments.

Kinetics studies were carried out at 20°C in the Zn(II) solution with 26.15 mg/L concentration at various time intervals between 5 and 180 min. Isotherm experiments were performed in Zn(II) solution with various initial concentrations ranging from 5.25 to 78.45 mg/L, at 10, 20 and 55.5°C, and a contact time of 3 h.

CONCLUSIONS

In this study, the sawdust obtained as waste from wood processing industry was used for the removal of Zn(II) ions from aqueous solutions, in batch systems. The study of influencing parameters has shown that the Zn(II) removal occurs with maximum efficiency at initial solution pH of 1.09 and 6.23, 8.0 g sawdust/L, 100 min of contact time and ambient temperature. The equilibrium data were well described by Langmuir model and the values of maximum adsorption capacity were 2.38 mg/g at pH of 1.09 and 7.20 mg/g at pH of 6.23, respectively. The kinetic data have shown that the equilibrium stage was quickly achieved and could be described by the pseudo-second order kinetic model. The thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) calculated from experimental results have indicated that the adsorption process is thermodynamically favourable and endothermic. The results presented in this study indicate that the sawdust can be considered a viable alternative for the removal of Zn(II) ions from aqueous solutions, and its utilization for this purpose is in agreement with the principles of sustainable development.

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