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Removal of Zn(II) ions from aqueous media on thermal activated sawdust

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ABSTRACT

The adsorptive characteristics of thermal activated sawdust were examined for the removal of Zn(II) ions from aqueous solution. Batch experiments were performed in order to study the influence of initial Zn(II) concentration and contact time under optimal experimental conditions (initial solution pH of 1.09 and 6.23, 8.0 g/l) and the results were compared with those obtained on non-activated sawdust. A significant increase in adsorption capacity of thermal activated sawdust for Zn(II) ions, with 77.19% at pH 1.09 and with 395.12% at pH 6.23, was obtained at highest Zn(II) initial concentration of 78.50 mg/L. The equilibrium data of Zn(II) adsorption onto non-activated sawdust are very well described by the Langmuir model, while in case of Zn(II) adsorption onto thermal activated sawdust, the Freundlich model is more suitable for the fitting of experimental data. From kinetic point of view, the Zn(II) adsorption on thermal activated and non-activated sawdust attains the maximum after 60 min of contact time and follows the pseudo-second-order mechanism. The thermal activated sawdust has incontestable improved adsorptive characteristics for Zn (II) removal from aqueous solutions.

Keywords: Sawdust; Thermal activation; Zn(II) ions; Adsorption; Isotherm; Kinetics

1. Introduction

The increase in heavy metals' concentration in the surface and ground waters is mainly due to the effluent discharges from industrial activities. Generally, in most of the industrial effluents, the heavy metals' content exceeds the maximum permissible limits, and therefore, their discharge has negative impact on environment, with serious health and ecological consequences [1].

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Even though the zinc is considered an essential element for growth and metabolism of living organisms [2], its various utilization in industrial activities (such as electroplating, metal processing, paint and pigments production and fertilizers manufacturing) [3] has contributed to the contamination of water sources with this heavy metal. Because in most of the cases, its concentration exceeds the amount required for correct biological functioning [4], the pollution of waters with zinc has become a serious issue. Therefore, to ensure the quality of environment, the removal of Zn(II) ions from industrial effluents is required, and this could be also important from economical considerations, mainly due to the industrial importance of this metal ion.

Various methods, such as chemical precipitation, ion exchange, electrochemical techniques, adsorption and membrane-related processes, [5–7] are applied for the removal of Zn(II) ions from industrial effluents, at a small or larger scale. Among these methods, the adsorption has become one of the most preferred in many cases [1] due to its high efficiency, simplicity, ease of operation, minimization of secondary wastes, quantitative recovery of retained metal ion and low cost [8,9].

A wide range of natural materials and agricultural or industrial wastes have been tested for adsorptive removal of Zn(II) ions from aqueous solutions, in various experimental conditions [10–14], including sawdust. Although many studies from literature [15–17] have pointed out the adsorptive properties of this material for the removal of different metal ions from aqueous solutions, its main use is still as fuel for thermal energy generation, even if the efficiency of conversion systems is relatively low. Usually, the sawdust resulted from wood processing industry is densified into briquettes, in order to provide more energy per unit of volume, to improve transportation and storage [18] and used to heat houses and production areas.

In the last year, it has proved that the use of cellulosic wastes as sawdust in gasification processes could significantly improve the efficiency of energy production [19]. Generally, during gasification, the organic part of sawdust is transformed into gases, which may be then used to obtain energy in turbines or boilers. The utilization of sawdust in gasification processes has two major advantages: (i) the volume of sawdust waste is considerable reduced, which represents an important benefit for environment, and (ii) the cost of energy production is lower in comparison with classical combustion methods, because these processes generally occur at relatively low temperatures (until 700°C) and in low-oxygen atmosphere [19,20]. The solid residue remained after gasification, called tar or ash, is generally stored in controlled conditions, although in literature is mentioned the possibility of its use as building material, fertilizer, or in glass manufacture [21]. On the other hand, such tar has structural and textural characteristics which recommend him as potential adsorbent material in decontamination processes of environment.

In this study such tar, named thermal activated sawdust, obtained after sawdust gasification has been used as adsorbent for the removal of Zn(II) ions from aqueous solutions. The adsorptive performances of thermal activated sawdust have been tested in batch experiments in comparison with non-activated sawdust and followed the influence of initial Zn(II) concentration and contact time on the efficiency of adsorption process, under optimal conditions (pH 1.09 and 6.23, 8 g/L adsorbent dose), established previously [22]. The experimental data have been analysed using three isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich) and three kinetic models (pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model). The parameters calculated for each case, have permitted the selection of most suitable isotherm and kinetic model for the adsorption of Zn(II) ions onto non-activated and thermal activated sawdust.

2. Experimental

2.1. Materials

The sawdust used for adsorption studies was purchased from a local wood processing company (Moldsilva Suceava, Romania), and it is a waste obtained from processing of various coniferous wood species. The sawdust samples were washed several times with distilled water to remove impurities, dried in oven at 75–80°C for 6 h, mortared and stored in desiccators for further use.

The thermal activation of sawdust was done by heating the sawdust samples at 350°C for 4 h in a low-oxygen atmosphere, using a Nabertherm-GmbH oven. These conditions have been chosen based on derivatogram curves recorded for sawdust (Mettler 851 Derivatograph) (data not shown). The weight loss of sawdust after thermal activation was by 89.39%, which recommends this material as potential feedstock in gasification processes. After thermal activation, the obtained material was cooled at room temperature, mortared and used in adsorption experiments. The modifications that appear in the structure of sawdust after thermal activation have been highlighted by FT-IR spectra, recorded before and

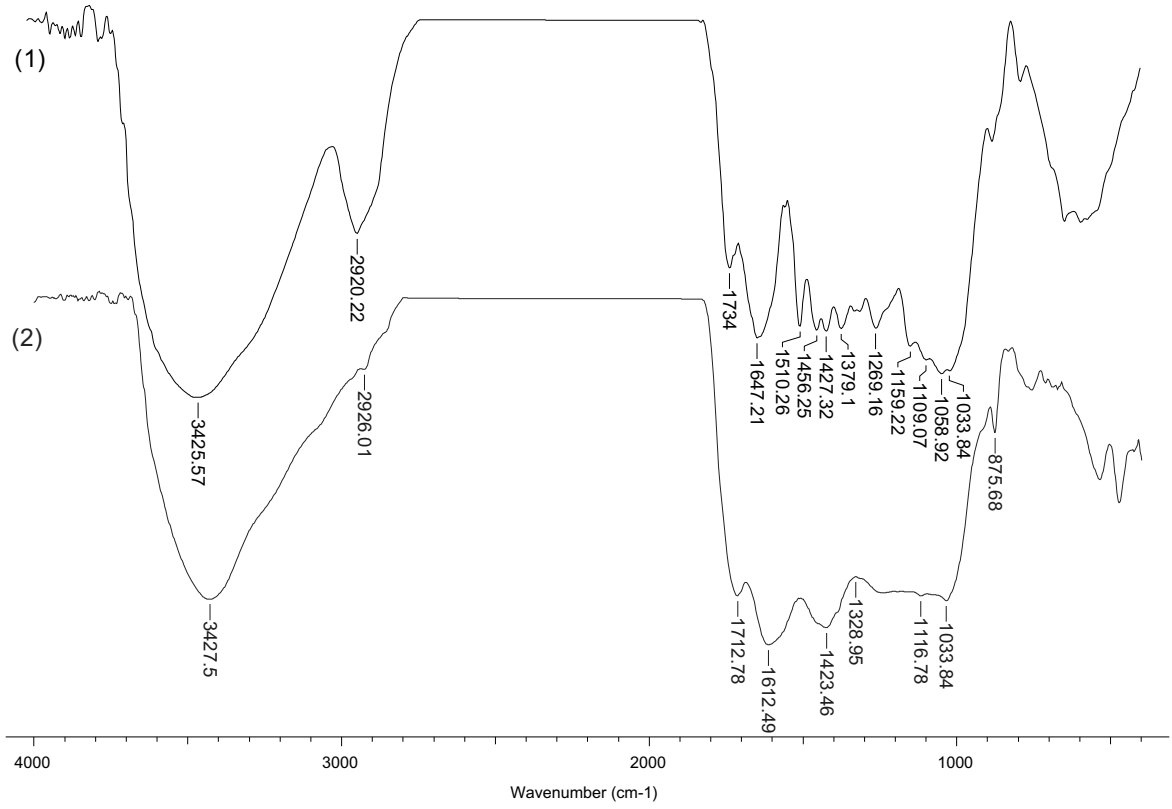

Fig. 1. FT-IR spectra of non-activated (1) and thermal activated (2) sawdust.

after thermal treatment (Bio-Rad FT-IR Spectrometer, 400–4,000 cm^{-1} spectral domain, 4 cm^{-1} resolution, by KBr pellet technique), and the analysis of FT-IR spectra was carried out by examining the spectral bands that are modified.

All chemical reagents were of analytical grade and were used without further purifications. In all experiments, distilled water obtained from a commercial distillation system was used for the preparation and dilution of solutions.

The stock solution of Zn(II) (containing 654 mg 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. The initial pH values of working solutions were obtained using 0.1 mol/l HNO_3 and NaOH solutions. Fresh dilutions were prepared and used for each experiment.

2.2. Adsorption experiments

The adsorption experiments were performed in batch system at room temperature (22 ± 0.5˚C) by mixing adsorbent samples (thermal activated and non-activated sawdust) of 0.2 g with 25 ml of Zn(II) solution with known concentration (5.25–78.50 mg/l), at initial solution pH of 1.09 and 6.23. The values of initial solution pH (1.09 and 6.23) and adsorbent dose (8.0 g/l) were established in a previous study [22] as optimal for Zn(II) adsorption onto sawdust. The kinetic experiments were carried out using constant adsorbent samples (0.2 g) and 25 ml of Zn(II) solution with 26.16 mg/l concentration at various time intervals between 5 and 180 min. After the adsorption experiments were finished, the solid and liquid phases were separated by filtration on quantitative filter paper, and Zn(II) concentration in filtrate was spectrophotometrically analysed with xylenol orange (Digital Spectrophotometer S104D, $\lambda = 570$ nm, 1 cm glass cell, against distilled water), using a prepared calibration graph.

The adsorption capacity (q, mg/g) of non-activated and thermal activated sawdust for Zn(II) ions was calculated from experimental data, according to the relation:

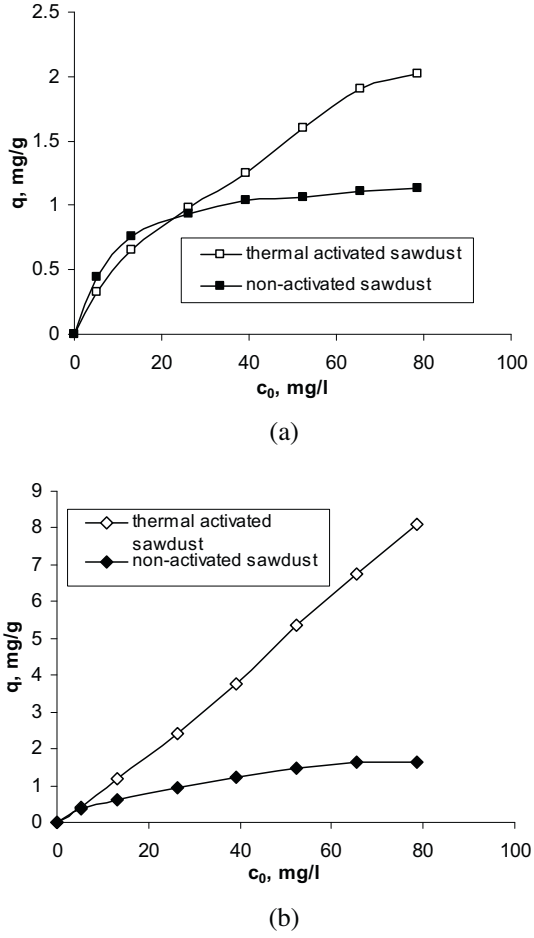

Fig. 2. Effect of initial Zn(II) concentration on the adsorption onto non-activated and thermal activated sawdust ((a): pH 1.09; (b): pH 6.23; 8 g/l adsorbent dose, 24-h contact time; 22°C).

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (1)$$

where c_0 is the initial concentration of Zn(II) solution (mg/l), c is the equilibrium concentration of Zn(II) solution (mg/l), V is volume of solution (ml) and m is the adsorbent mass (g).

3. Results and discussion

3.1. Characterization of the adsorbent materials

FT-IR spectra (Fig. 1) recorded for sawdust before and after thermal treatment were used to highlight the potential use of these materials as adsorbents.

Thus, in case of non-activated sawdust (spectra 1), the most important functional groups are aliphatic and aromatic hydroxyl groups (3,425 cm^{-1}), aliphatic radicals (2,920 cm^{-1}), carboxyl groups (1,734 cm^{-1}), carbonyl and ether groups (1,647 cm^{-1}), aromatic radicals with branched structure (1,510–1,427 cm^{-1}), C–O groups from organic carboxyl compounds and their derivates or syringyl rings (1,159–1,033 cm^{-1}). All these functional groups are potential binding sites and may interact with Zn(II) ions during adsorption process.

After thermal treatment, the FT-IR spectra of thermal activated sawdust (spectra 2) show that the splitting degree of adsorption peaks significantly decreases and this is mainly determined by the destruction of physical bonds between functional groups from sawdust structure. Moreover, after thermal activation, most of the functional groups are passed in their reduced form, predominantly being here hydroxyl groups (3,427 cm^{-1}) and carbonyl or ether groups (1,612 cm^{-1}). Another significant difference is the drastic reduction in the intensity of peak from 2,926 cm^{-1} that correspond to the C–H stretching vibration of aliphatic hydrocarbons radicals. The significant decrease in this peak shows that after thermal treatment, most of the aliphatic hydrocarbons chains from sawdust structure were removed by burning (probably as CO_2 and H_2O), and in composition of resulted material remains predominantly aromatic scraps.

Analysing the differences from FT-IR spectra, it can be observed that in the structure of thermal activated sawdust are still sufficient functional groups which allow the binding of Zn(II) ions from aqueous solutions. In addition, its more relaxed structure in comparison with non-activated sawdust may be also a considerable advantage in adsorption processes.

3.2. Effect of initial Zn(II) concentration and equilibrium modelling

The effect of initial Zn(II) concentration on the adsorption capacity of thermal activated and non-activated sawdust is illustrated in Fig. 2. Adsorption experiments were carried out by varying initial Zn(II) concentration from 5.25 to 78.50 mg/l under optimal conditions (initial solution pH of 1.09 and 6.23, 8.0 g/l adsorbent dose) established previously.

The experimental results have showed that in comparison with non-activated sawdust, the thermal activated sawdust has higher adsorption capacity on entire studied concentration range and for both values of initial solution pH. Even if the adsorption efficiency of both adsorbent materials increases with the increasing in initial Zn(II) concentration, mainly due to the increasing in interaction probability between Zn

Table 1
Mathematical equations of Langmuir, Freundlich and Dubinin–Radushkevich isotherm models [23–25]

Isotherm model	Mathematical equation	Notations	Observations
Langmuir	$\frac{c}{q} = \frac{c}{q_{max}} + \frac{1}{q_{max} \cdot K_L}$	q—the amount of Zn(II) retained on weight unit of adsorbent at equilibrium	Adsorption occurs until a complete monolayer coverage is formed at the surface of adsorbent
		q_{max}—the maximum adsorption capacity	Is useful in the estimation of q_{max} (mg/g) that correspond to the surface saturation
		K_L—the Langmuir constant	
Freundlich	$\log q = \log K_F + \frac{1}{n} \cdot \log c$	K_F—Freundlich constant	Adsorption occurs on heterogeneous surface and is not restricted to the formation of a monolayer
		n—the heterogeneity factor	Used for the estimation of adsorption intensity
Dubinin–Radushkevich	$\ln q = \ln q_m^{D-R} - \beta \cdot \varepsilon^2$	q_m^{D-R}—maximum amount of Zn(II) ions retained on mass unit of sawdust (mg/g)	Gives information about the nature (physical or chemical) of interactions between metal ions and functional groups of adsorbent
	$E = \frac{1}{\sqrt{-2\beta}}$	β—constant related to adsorption energy (mol^2/kJ)	
		ε—the Polanyi potential	
		E—mean biosorption energy (kJ/mol)	

(II) ions and superficial functional groups of adsorbents, this variation is more pronounced in case of thermal activated sawdust, and it is more evident at high initial Zn(II) ions concentration. Therefore, if for lowest initial Zn(II) concentration (5.25 mg/l), the adsorption capacity of thermal activated sawdust increases only with 3.12% at pH of 1.09 and with 11.43% at pH of 6.23 in comparison with non-activated sawdust, at higher initial Zn(II) concentration (78.50 mg/l), this increase is over 77% at pH of 1.09 and 395% at pH of 6.23, respectively.

This significant improvement of sawdust adsorption capacity after thermal activation is probably determined by two main factors: (i) the breaking of physical bonds between functional groups from sawdust surface, resulting in the increase in their availability to interact with metal ions from aqueous solution through chemical interactions (ion exchange type), and (ii) the relaxation of adsorbent material structure as a result of the combustion of aliphatic hydrocarbon radicals, which favours the binding of metal ions from aqueous solution by physical interactions (hydrogen bonds).

In order to characterize the isotherms obtained for Zn(II) ions adsorption onto non-activated and thermal activated sawdust, three isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich) have been used. The mathematical equations of these three models in their linear forms are presented in Table 1 [23–25]. The choice of these models was done considering their usefulness in the description of adsorption process, and these arguments are also mentioned in Table 1.

The isotherm parameters for each model were calculated from the slopes and intercepts of their linear representations (Fig. 3), and the obtained values together with the values of regression coefficients (R^2) are summarized in Table 2.

As can be seen from Table 2, in case of non-activated sawdust, the regression coefficients of Langmuir model were higher than the regression coefficients of Freundlich and Dubinin–Radushkevich models, while in case of thermal activated sawdust, the regression coefficients of Freundlich model were higher than those obtained for Langmuir and Dubinin–Radushkevich models, for both initial solution pH. This indicates that the adsorption of Zn(II) ions on non-activated sawdust occurs on monolayer and it is well described by Langmuir model, while in case of thermal activated sawdust, the Freundlich model is more suitable for the characterization of Zn (II) adsorption process, indicating multilayer adsorption that occurs on a heterogeneous adsorbent surface. Also, the values of q_{max}, which represents the maximum amount of Zn(II) ions required to form a compete monolayer coverage, are comparable with those obtained experimental in case of non-activated sawdust (1.13 mg/g for pH of 1.09 and 1.65 mg/g

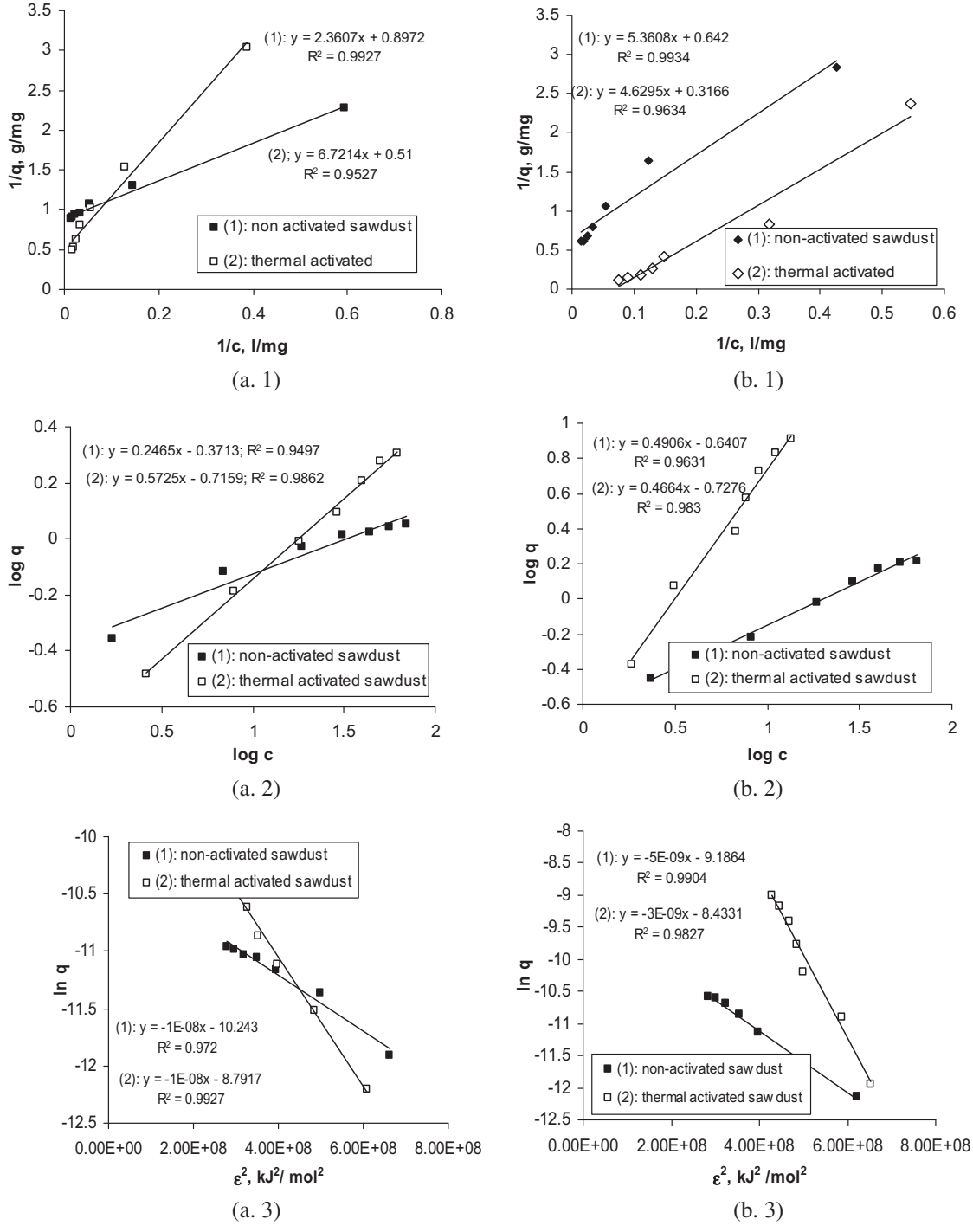

Fig. 3. Linear representations of Langmuir (1), Freundlich (2) and Dubini–Radushkevich (3) isotherm models for Zn(II) adsorption onto non-activated and thermal activated sawdust at pH of 1.09 (a) and 6.23 (b).

for pH of 6.23, respectively), but are much lower in case of thermal activated sawdust (2.56 mg/g for pH of 1.09 and 8.12 mg/g for pH of 6.23, respectively). This is another argument which sustains the hypothesis that the adsorption of Zn(II) ions takes place after different mechanism onto non-activated and thermal activated sawdust, in mentioned experimental conditions.

This different adsorption behaviour is probably determined by the relaxed structure of adsorbent after

Table 2
Isotherm parameters for the adsorption of Zn(II) ions onto non-activated and thermal activated sawdust

Isotherm model	Parameter	Non-activated sawdust		Thermal activated sawdust	
		pH = 1.09	pH = 6.23	pH = 1.09	pH = 6.23
Langmuir	R^2	0.9927	0.9934	0.9827	0.9634
	q_{max}, mg/g	1.1145	1.5576	1.9608	3.1586
	K_L, dm^3/mg	0.3801	0.1198	0.0758	0.0684
Freundlich	R^2	0.9497	0.9734	0.9962	0.9937
	$1/n$	0.2465	0.4906	0.5725	0.4664
	K_F, (mg/g) $(dm^3/mg)^{1/n}$	0.6898	0.5269	0.4887	0.4831
Dubinin–Radushkevich	R^2	0.9720	0.9904	0.9927	0.9827
	q_m^{D-R}, mg/g	2.3275	6.6953	9.9355	14.2209
	E, kJ/mol	7.1803	14.1421	7.9978	18.2574

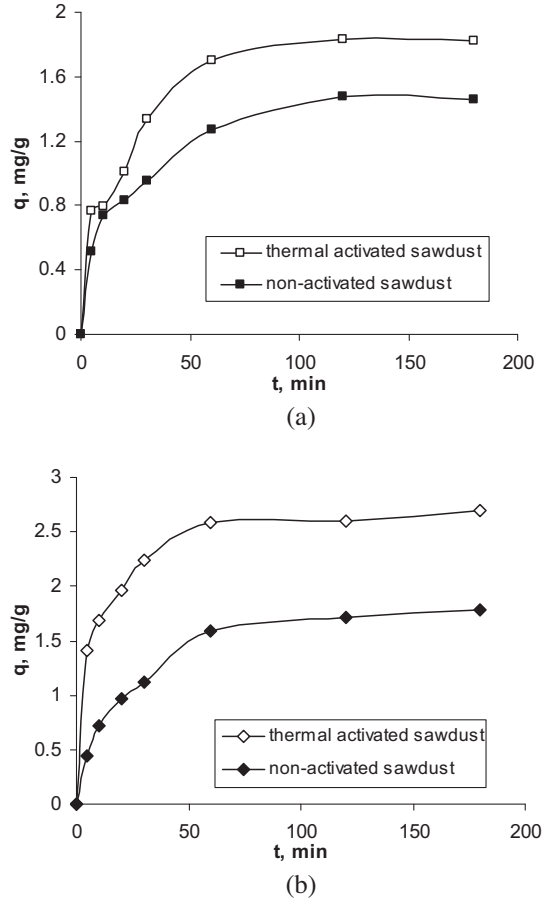

Fig. 4. Effect of contact time for Zn(II) adsorption onto non-activated and thermal activated sawdust ((a) pH 1.09; (b) pH 6.23; 8 g/l adsorbent dose; c_0 = 26.16 mg/l; 22°C).

thermal activation. The burning of aliphatic hydrocarbon chains proved by FT-IR spectra (Fig. 2—spectra 2) leads to the increase in pores dimensions, which will facilitate the entering of Zn(II) ions inside of adsorbent material particles. This makes possible the retention of Zn(II) ions on thermal activated sawdust in multilayer, and thus the adsorption process to be described by Freundlich isotherm model. In case of non-activated sawdust, the existence of physical bonds between functional groups, also proved by FT-IR spectra (Fig. 2—spectra 1), prevents the penetration of Zn(II) ions inside of adsorbent material particles, and in consequence, the adsorption process occurs only at sawdust surface, being well described by Langmuir model.

It should be also noted that the adsorption of Zn(II) ions is a favourable process even at high initial metal ions concentration for both adsorbent materials and initial solution pHs, since the $1/n$ parameter from Freundlich model has values between 0 and 1 in all cases, but the type of interactions involved in adsorption process are different, depending on the initial solution pH. Thus, the values of mean adsorption energy (E, kJ/mol) calculated from Dubinin–Radushkevich isotherm model are close to 8 kJ/mol when initial solution pH is 1.09, and between 8 and 15 kJ/mol in case of initial solution pH of 6.23, both for non-activated and thermal activated sawdust. This means that in strong acidic medium (pH 1.09), the adsorption of Zn(II) predominantly occurs by physical interactions, probable hydrogen bonds, while in weak acidic/neutral medium (pH 6.23), the retention of

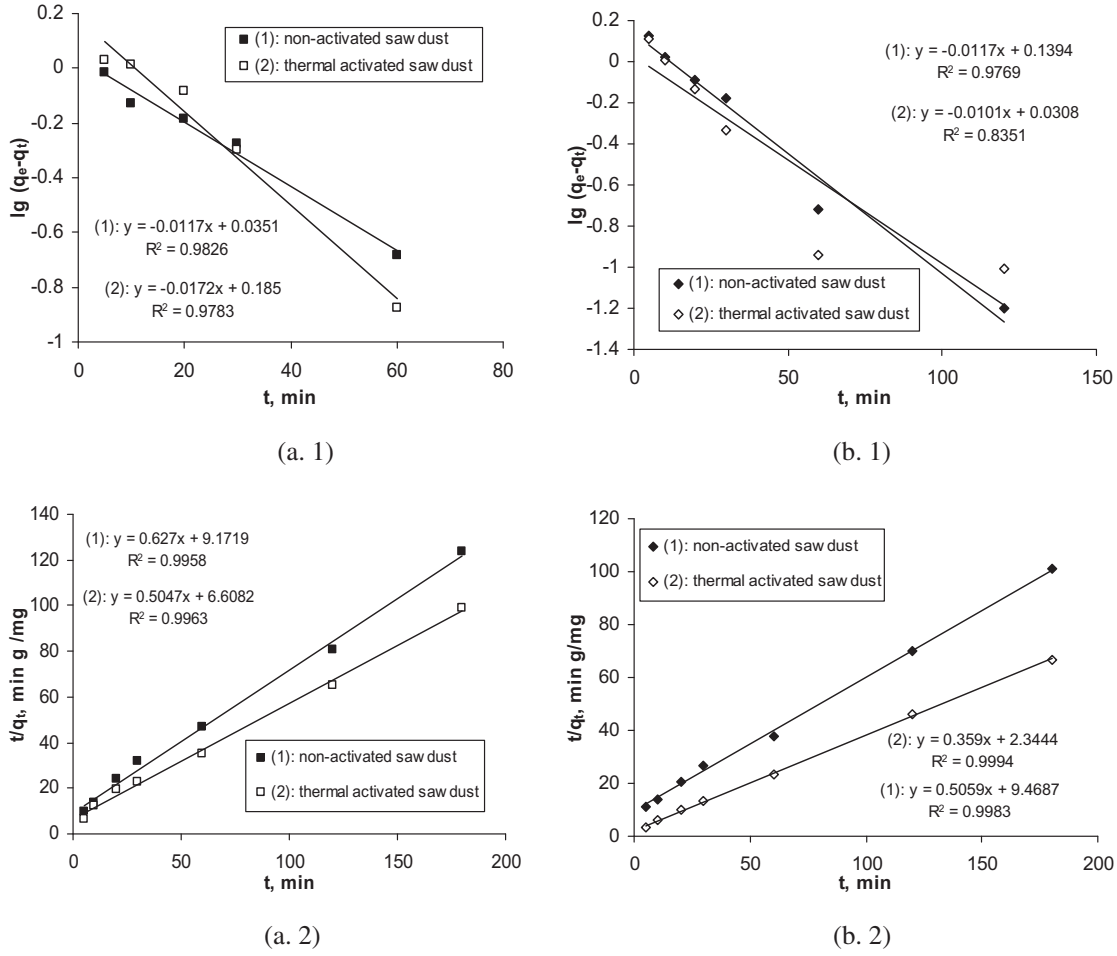

Fig. 5. Linear representations of pseudo-first (1)- and pseudo-second (2)-order kinetics models for the adsorption of Zn(II) ions onto non-activated and thermal activated sawdust at pH of 1.09 (a) and 6.23 (b).

Zn(II) ions involves chemical interactions, probable ion exchange between metal ions and dissociated functional groups [26]. This significant difference in adsorption mechanism of Zn(II) ions onto non-activated and thermal activated sawdust as a function of initial solution pH has very important consequences in practical utilization of this adsorption process at large scale.

3.3. Effect of contact time and kinetics modelling

The influence of the contact time on the adsorption efficiency of Zn(II) ions onto non-activated and thermal activated sawdust, for both values of initial solution pH, is illustrated in Fig. 4.

For an initial Zn(II) concentration of 26.16 mg/l, the adsorption efficiency of Zn(II) drastically increases within first 60 min and then reaches its maximum, for all studied cases. As expected, the amount of Zn(II) retained after equilibrium state is reached depending on the type of adsorbent material (being higher in case of thermal activated sawdust than in case of non-activated sawdust) and on the value of initial solution pH (the adsorption process is more efficient at pH 6.23 than at pH 1.09).

In order to investigate the adsorption mechanism of Zn(II) ions onto non-activated and thermal activated sawdust, three kinetic models (pseudo-first order, pseudo-second order and intra-particle diffusion model) were used to test the experimental data. The linear equations of these models [27,28] and the values of kinetic parameters calculated from the slopes and intercepts of each linear representation (Fig. 5) are summarized in Table 3.

As observed from Table 3, the Zn(II) ions adsorption onto non-activated and thermal activated sawdust was better described by the pseudo-second-order

Table 3
Kinetics parameters for the adsorption of Zn(II) onto non-activated and thermal activated sawdust [27,28]

Kinetic model	Equation	Parameter	Non-activated sawdust				Thermal activated sawdust			
			pH = 1.09		pH = 6.23		pH = 1.09		pH = 6.23	
Pseudo-first order	$\log(q_e - q_t) = \log q_t - k_1 \cdot t$	q_e^{exp}, mg/g	1.4811		1.7815		1.8236		2.7011	
		R^2	0.9826		0.9769		0.9783		0.8351	
		q_e^{calc}, mg/g	1.0842		1.3785		1.5311		1.0735	
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	k_1, 1/min	0.0117		0.0117		0.0172		0.0101	
		R^2	0.9958		0.9983		0.9963		0.9994	
		q_e^{calc}, mg/g	1.5949		1.9766		1.9814		2.7855	
Intra-particle diffusion model	$q_t = k_{diff} \cdot t^{1/2} + c$	k_2, g/mg min	0.0683		0.0534		0.0763		0.1531	
		Region	I	II	I	II	I	II	I	II
		R^2	0.9353	0.7249	0.9781	0.9854	0.9048	0.7554	0.9974	0.7988
		k_{diff}, mg/g min$^{1/2}$	0.1256	0.0338	0.2059	0.0343	0.1739	0.0225	0.2500	0.0196
		C, mg/l	0.2746	1.0421	0.0225	1.3287	0.3099	1.5451	0.8663	2.4206

Notations: q_e, q_t—the amounts of Zn(II) retained on weight unit of adsorbent at equilibrium and at time t; k_1—the rate constant of pseudo-first-order kinetics equation; k_2—the pseudo-second-order rate constant; k_{diff}—the intra-particle diffusion rate constant; c—the concentration of Zn(II) ions from solution at equilibrium; superscript I and II—region I and region II, respectively, from intra-particle diffusion model.

kinetic model, for both initial solution pHs, since the regression coefficients (R^2) of this model have the highest values. This is also confirmed by the values of q_e^{calc} from pseudo-second-order kinetic equation that are very close to the values obtained experimental (q_e^{exp}, mg/g). This means that in case of Zn(II) adsorption onto non-activated and thermal activated sawdust, the rate limiting step of the adsorption process involves chemical interactions (ion exchange and/or sharing of electrons) between Zn(II) ions from aqueous solution and functional groups of adsorbent [29], and this is applied for both values of initial solution pH.

If for systems with initial solution pH of 1.09, the retention of Zn(II) ions through the hydrogen bonds occurs with almost same probability both on non-activated and thermal activated sawdust since the values of rate constant (k_2) are close, in case of systems with initial solution pH of 6.23, the achievement of ion exchange interactions is more facile when thermal activated sawdust is used as adsorbent (the rate constant is with one order of magnitude higher than for non-activated sawdust). This is probable because after thermal treatment of sawdust, its functional groups become more available to interact with Zn(II) ions from aqueous solution, and the adsorption process occurs more faster. In consequence, even if the time required to reach the equilibrium state is almost the same for both adsorbent materials (see Fig. 4), the amount of Zn(II) ions retained is higher in case of thermal activated sawdust than in case of non-activated sawdust.

On considering the adsorption systems, the intra-particle diffusion is not the rate limiting step, since the plots of q vs. $t^{1/2}$ (Fig. 6) do not pass through the origin and two separated regions can be delimitated in each case. The deviation of straight lines from origin indicates that the boundary layer diffusion controls the Zn(II) adsorption up to a certain degree.

According to the studies from literature [30,31], the first region (region I) corresponds to the mass transfer effects that take place in the boundary layer diffusion, while the second region (region II) indicates the intra-particle diffusion into the pores of adsorbent material. The higher slopes of the first region than the slopes of second region for both adsorbent materials suggest that the binding sites are located at the surface or at the external interlayer surface and are accessible for metal ions. In consequence, the intra-particle diffusion influences the adsorption process, and that this influence is effective after 60 min of contact time, when the rate of adsorption process is slower.

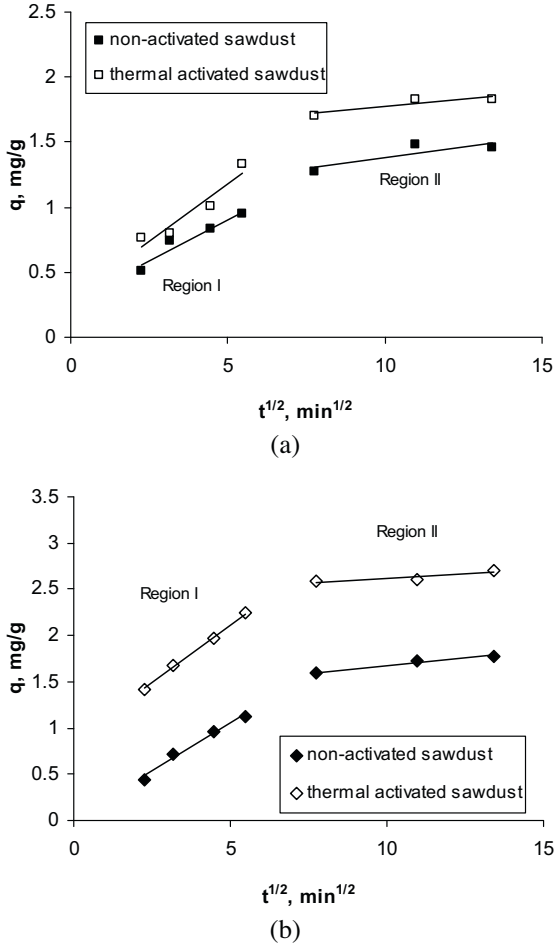

Fig. 6. Intra-particle diffusion kinetics for the adsorption of Zn(II) onto non-activated and thermal activated sawdust, at pH of 1.09 (a) and 6.23 (b).

3.4. Comparison of thermal activated sawdust with other adsorbents

As was mentioned before, one of the possibilities of reuse of sawdust obtained as waste from wood processing industry is its utilization in gasification processes for energy production [19]. The solid residue remained after gasification, named in this study thermal activated sawdust, is mostly controlled deposited, or due to his textural and structural properties, can be used as an alternative adsorbent in environment decontamination. In order to highlight the practical applicability of thermal activated sawdust in the Zn(II) removal processes, the adsorption capacity of the sawdust, before and after thermal treatment, was compared with those of other similar adsorbents reported in the literature (Table 4).

It can be observed that the maximum adsorption capacity of the sawdust for Zn(II) ions is lower than most of the values reported for different kinds of sawdust adsorbents, which explains its limited utilization as adsorbent for the removal of heavy metal ions from aqueous solution. However, in case of thermal activated sawdust, the values of maximum adsorption capacity are comparable with those obtained for adsorbents derived from cellulosic materials before and after thermal treatments, tested for Zn(II) removal in similar experimental conditions. Therefore, the thermal activated sawdust can be used as a potential adsorbent in removing of Zn(II) ions from aqueous media, and this alternative could be also a suitable solution for the sustainable use of wastes obtained from gasification processes.

Table 4
Comparative values of maximum adsorption capacities for Zn(II) ions of different various adsorbent materials

Adsorbent	pH	q_{max} (mg/g)	Refs.
Corn husks	7.50	6.80	[12]
Poplar sawdust	6.00	5.10	[15]
Fir sawdust	6.00	6.11	[15]
Bamboo sawdust	5.00	107.52	[32]
Surfactant modified bamboo sawdust	5.00	104.17	[33]
Sawdust	1.09	1.13	This study
	6.23	1.65	
Corn straw char	5.00	11.00	[34]
Hard wood char	5.00	4.00	
Empty fruit branch magnetic biochar	10.00	1.18	[35]
Thermal activated sawdust	1.09	2.56	This study
	6.23	8.12	

4. Conclusions

In this study, the adsorptive characteristics of thermal activated sawdust were investigated for the removal of Zn(II) ions from aqueous solutions, in comparison with non-activated sawdust. The experiments were performed in batch systems as a function of initial Zn(II) concentration and contact time, under optimal experimental conditions (pH of 1.09 and 6.23, 8.0 g/l adsorbent dose) established previously. A significant increase in adsorption capacity of sawdust for Zn(II) ions was obtained after thermal activation (with 77.19% at pH of 1.09 and with 395.12% at pH of 6.23, respectively), while the contact time required to attain the equilibrium state remains the same (about 60 min) for both adsorbent materials. Three isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich) were used to analyse the experimental data obtained for Zn(II) ions adsorption onto non-activated and thermal activated sawdust. The results indicate that in case of non-activated sawdust, the adsorption equilibrium data are very well described by the Langmuir model, while in case of thermal activated sawdust, the Freundlich model is more suitable for the fitting of experimental data. This different adsorption behaviour is probably determined by the relaxed structure of adsorbent after thermal activation, which determines the increase in pores dimensions and makes possible the retention of Zn (II) ions onto thermal activated sawdust in multilayer. The adsorption process of Zn(II) ions onto non-activated and thermal activated sawdust follows the pseudo-second-order kinetic model, both for pH of 1.09 and 6.23, respectively. This means that the rate limiting step of the adsorption process involves chemical interactions (ion exchange and/or sharing of electrons) between Zn(II) ions from aqueous solution and functional groups of adsorbent, and the type of interactions depends on the value of initial solution pH. The results of this study indicate that thermal activated sawdust has incontestable improved adsorptive characteristics than non-activated sawdust and could be successfully used for the efficient removal of Zn(II) ions from aqueous solutions.

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