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Utilization of wood-industrial waste material as potential adsorbent for the removal of Zn (II) and Cu (II) from aqueous single metal solutions

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

In this research, we have described the ability of fir tree sawdust, a waste material derived from wood-industrial processing, for the removal of Zn (II) and Cu (II) from aqueous single metal solutions. Batch experiments were carried out to investigate the effect of significant process parameters, such as biomass quantity, initial pH, temperature and initial concentration of metals. The optimum initial pH for adsorption was 7.4 for Zn (II) and 6.4 for Cu (II). Kinetics data obtained during adsorption of both metals were best described by the pseudo-second-order model. The equilibrium data for the adsorption of Zn (II) and Cu (II) onto sawdust were tested with four adsorption isotherm models, including the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin. The thermodynamic parameters determined for each metal indicated that the adsorption process is endothermic in nature. FTIR analysis was conducted to characterize the biosorbent and to understand which functional groups were responsible for the metal binding process.

KEYWORDS
adsorption; isotherms; kinetics; metal ions; sawdust; thermodynamics

1. INTRODUCTION

Global industrialization entails several environmental problems, including water pollution with heavy metals, which are considered dangerous due to their high level of toxicity, persistence and non-biodegradability. Heavy metals such as Cd, Hg and Pb are well-known ecotoxicological hazardous substances. Their accumulation can become extremely dangerous to living beings. While other metals like Cu, Zn, Mn, Fe, Ni and Co are essential for animals and plants, but in excessive concentrations and above certain limits they can also become very harmful for living organisms.

Zinc is one of most important metals present in high concentrations in the wastewaters of pharmaceutical, galvanizing, paints and pigments, cosmetics industries etc., causing severe problems to humans and their environment (Naiya et al., 2009). Zinc toxicity has been found in both acute and chronic forms with symptoms including loss of appetite, nausea and irritability.

Copper may also be present in industrial wastewater from metal-process pickling baths and plating baths, but also from a variety of chemical manufacturing processes employing copper salts or copper catalyst (Acar and Eren, 2006). Copper causes serious health issues to humans (e.g. stomach intestinal distress, kidney damage and anemia), microorganisms (disruption of plasma membrane integrity) and animals (carcinogenic effect) (Rahman and Islam, 2009).

The pollution of water resources due to a careless disposal of these toxic metals has been causing worldwide concern for the past few decades. There-

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fore, researchers strive to develop new, effective, fast, precise and cost effective processes for the removal of heavy metals from wastewaters. A number of conventional removal methods are known today: chemical precipitation (Du Pont, 1987), reverse osmosis (Hanra and Ramachandhra, 1996), coagulation (Chang and Wang, 2007), ion-exchange (Rengaraj et al., 2003), membrane filtration (Sabry et al., 2007) and adsorption (Krishnan and Anirudhan, 2002). Among these methods, adsorption is considered the most flexible, easy to operate and efficient method which can remove high amounts of toxic metals. In these adsorption processes, different types of waste materials originating from forestry and agricultural activities were tested and used: fly ash (Wang and Wu, 2006), wood bark (Shin et al., 2007), rice husk (Kumar and Bandyopadhyay, 2006), tea waste (Cay et al., 2004), maize bran (Singh et al., 2006) and different types of sawdust (Semerjan, 2010; Nagy et al., 2013; Božić et al., 2013). Sawdust, with high cellulose and hemicellulose contents is a cheap, widely available and abundant natural material, which has been employed as adsorbent for different metal ions present in wastewaters. In Romania, fir (*Abies* sp.) is used by both paper and furniture industry, so that every year a huge amount of fir tree sawdust is extracted for commodity production.

The main objective of the present study is to investigate the possible use of fir tree sawdust, a waste/by-product from wood industry, as an alternative adsorbent material for the removal of Zn (II) and Cu (II) from aqueous single metal solutions. We investigate the effect of various important parameters on the adsorption, such as biomass quantity, initial pH, temperature and the initial concentration of metals. Pseudo-first-order and pseudo-second-order kinetic models were used to evaluate the mechanism of adsorption. The Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models were used to fit the experimental equilibrium isotherm data.

2. MATERIALS AND METHODS

2.1. Adsorbent

Sawdust of fir tree (*Abies alba*) was collected from a local sawmill in Huedin, Cluj County, Romania. Prior to utilization, the adsorbent was washed several times with distilled water in order to eliminate surface impurities and dried at 105 °C for 24 h. Finally the dried biomass was grounded and sieved (400 – 600 μm mesh size). The sieved sawdust was then stored in an airtight box before its utilization. No further chemical treatments were considered at this stage.

2.2. Chemicals

The experiments of heavy metal ions adsorption on sawdust were performed using synthetic solutions of Zn (II) and Cu (II). The stock solutions, 1 g/L of Zn (II) and Cu (II) were prepared by dissolving $ZnSO_4 \times 7H_2O$ and $CuSO_4 \times 5H_2O$, separately, in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in the concentration range of 38 – 250 mg/L. HCl (0.1 M) and NaOH (0.1 M) volumetric solutions were used to adjust the solution's pH. All chemicals used were of analytical grade.

2.3. Fourier transform infrared spectroscopy (FTIR)

Fresh and used sawdust samples were subjected to FTIR analysis for both heavy metals. Sawdust samples were prepared by encapsulating 1.2 mg of finely grounded biomass particles in 300 mg of KBr. Infrared spectra were obtained using a JASCO 615 (Japan) FTIR spectrometer 500 – 4000 cm^{-1} (resolution, 2 cm^{-1}) and data were processed with ORIGIN PRO 8.5 software.

2.4. Experimental method

The adsorption experiments were performed in batch conditions, contacting various quantities of sawdust (1 – 5 g) at 700 rpm (magnetic stirring), with 100 mL aqueous solution of Zn (II) or Cu (II), at different initial concentrations (38 – 250 mg/L), at 296 K for 240 min, until the final equilibrium was reached. In order to determine the concentration of heavy metals and to establish the evolution of the removal process, samples of 100 μL were collected at different time intervals (0 – 240 min). After specified contact times, aliquots of the sawdust-metal aqueous solution were filtered using 45 μm cellulose syringe filter and the filtrates were analyzed using flame Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). In order to evaluate the amount of zinc and copper ions retained per unit mass of sawdust, the adsorption capacity (q_e) and removal efficiency (E (%)) were calculated using the following equations:

$$E, (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$q_e(mg/g) = \frac{(C_i - C_f) \quad V}{m} \tag{2}$$

where E (%) represents the efficiency, C_i and C_f the initial and final concentration of heavy metals (mg/L) in the aqueous solution, q_e (mg/g) represents the amount of heavy metals adsorbed onto unit weight of adsorbent, V (L) means the volume of heavy metal aqueous solution and m (g) is the adsorbent quantity.

The effect of the initial solution pH on the equilibrium uptake of Zn (II) and Cu (II) was analyzed over a 2.3 to 8.5 pH range. The initial pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions at the beginning of the experiments.

Experimental data were used to determine the equilibrium time, biomass quantity of the adsorbent, the optimum initial pH and temperature for maximum efficiency. Similarly, experimental data were used to establish isotherm and kinetic models and thermodynamic parameters. All experiments were repeated three times, the values presented were calculated using averaged concentration values.

2.5. Adsorption kinetics

2.5.1. Pseudo-first-order kinetic model (Lagergren)

Lagergren suggested a first-order equation for the adsorption of liquid/solid system based on solid capacity, which can be expressed as follows (Lagergren, 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e and q_t (mg/g) are the amounts of the heavy metals adsorbed at equilibrium and time t (min), respectively, and k_1 is the rate constant of the equation (1/min). The sorption rate constants (k_1) can be determined experimentally by the plotting of $\ln(q_e-q_t)$ vs. t.

2.5.2. Pseudo-second-order kinetic model (Ho's model)

Pseudo-second-order equations proposed initially by Ho and McKay are the most simplified and very frequently used kinetic equation. These equations are used to model the adsorption process for a wide range of solute-sorbent systems, including metal ions and natural sorbent (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{4}$$

where k_2 (g/mg.min) is the rate constant of the pseudo-second-order equation.

2.6. Adsorption equilibrium

2.6.1. Langmuir isotherm model

The Langmuir model is based on the assumption that the uptake occurs on a homogenous surface by monolayer adsorption without interaction between the adsorbed molecules (Freundlich, 1906). This model can be expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max} b} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

where q_e (mg/g) is the solid-phase adsorbate concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity corresponding to the monolayer adsorption capacity, C_e (mg/L) is the solute concentration in liquid phase at equilibrium and b is the adsorption equilibrium constant that is related to the apparent energy of adsorption.

2.6.2. Freundlich isotherm

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer adsorption (Langmuir, 1916) and is expressed by the equation:

$$\ln q_e = \log K_F + \frac{1}{n} \times \ln C_e \tag{6}$$

where K_F is related to adsorption capacity and n is related to intensity of adsorption. The $\ln q_e$ versus $\ln C_e$ plot allows the determination of the Freundlich constants.

2.6.3. Dubinin-Radushkevich (D-R) isotherm

The Dubinin-Radushkevich model is a semi-empirical equation where adsorption follows a pore filling mechanism by assuming that the process has a multilayer character. The linear presentation of the D–R isotherm equation (Dubinin, 1960) can be expressed by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

where, β is the activity coefficient related to adsorption mean free energy (mol^2/J^2) and ε is the Polanyi potential. Free energy E per molecule of adsorbate, which helps to distinguish between the physical and chemical adsorption of metal ions is given below:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

2.6.4. Temkin isotherm

The Temkin model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbent-adsorbate interactions and the adsorption is characterized by a uniform distribution of the binding energies, up to the maximum binding energy (Temkin and Pyzhev, 1940). The equation of this model is given below:

$$Q_e = B \ln A_T + B \ln C_e \tag{9}$$

$$B = \frac{RT}{b_T} \tag{10}$$

where, A_T is the Temkin isotherm equilibrium constant (g/L), b_T is Temkin isotherm constant and B is a constant related to the heat of adsorption (mol/J).

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

In order to investigate the major functional groups involved in the adsorption process and to determine the vibrational frequency changes of fresh (unloaded) and metal loaded sawdust, FTIR spectral analysis was carried out. The spectra are shown in Figure 1. Having analyzed and compared the loaded spectra of the two metal ions (Cu (II), Figure 1b and Zn (II), Figure 1c), it can be concluded that the Cu (II) loaded sample exhibits more significant changes and modifications.

A major change can be observed from the broad and strong band at the intervals 3416 cm^{-1} and 3444 cm^{-1}, indicating the presence of free and intermolecular-bounded amino and hydroxyl groups (N–H bonding of amino and O–H stretching of hydroxyl groups). The peaks around 2921 cm^{-1} for unloaded (Figure 1a) and with slight modifications at 2923 cm^{-1} for Cu (II) loaded (Figure 1b) can be assigned to the –CH stretching vibrations of the $–CH_3$ and $–CH_2$ functional groups. Zn (II) adsorption did not cause any kind of modification in this region of spectra.

The peaks at regions 1631 cm^{-1} and 1508 cm^{-1} for Zn (II) loaded (Figure 1c) and 1512 cm^{-1} and 1654 cm^{-1} for Cu (II) loaded (Figure 1b) were attributed to the C=O stretching absorption band of ketone, aldehyde and carboxyl groups, wherein a significant decrease in intensity of Cu (II) loaded spectra could be observed. The peaks identified at around 1268 cm^{-1} (unloaded), 1272 cm^{-1} (Cu (II) loaded) and 1267 cm^{-1} (Zn (II) loaded) belong to the surface C–O bond stretching of phenolic groups. The strong C–O bands at 1059 cm^{-1} and 1032 cm^{-1} for unloaded and Zn (II) loaded samples and a remarkable shift in this peak as loaded with Cu (II) it seems that this functional group strongly participates in metal binding.

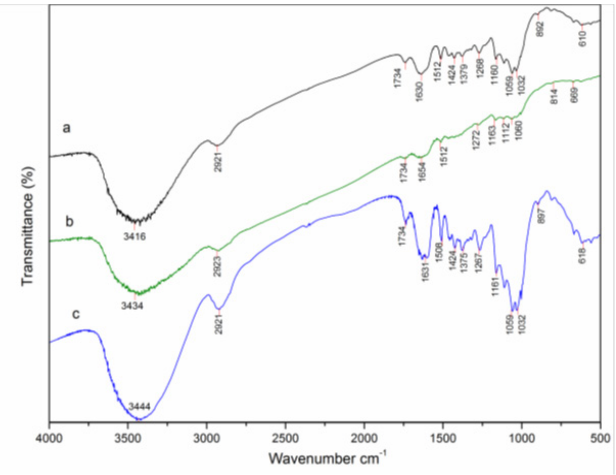

Figure 1. FTIR spectra analysis of fir tree sawdust before (unloaded) (a), after Cu (II) (b) and Zn (II) (loaded) (c) adsorption.

The peaks identified in the < 900 cm^{-1} region can be assigned to the sulfonate, phosphate and sulfide groups present in the sawdust. The significant modifications observable in the spectra for Cu (II) when compared with the spectra for the Zn (II) were in compliance with the obtained high adsorption capacity and removal efficiency for Cu (II). Similar FTIR results were reported in the scientific literature for the adsorption of heavy metals using sawdust from different wood species (Rahman and Islam, 2009; Zakaria et al., 2009; Chakravarty et al., 2010; Kapur and Mondal, 2013).

3.2. Effect of biomass quantity

The effect of sawdust quantity, varying from 1 to 5 g, on Zn (II) and Cu (II) adsorption is presented in Figure 2. The increase of Zn (II) and Cu (II) removal efficiency with the increase of biomass quantity is due to the availability of greater surface area and more adsorption sites. As sawdust quantity was increased from 1 to 5 g (in both cases), removal efficiency increased from 15.26% to 72.37% (for Zn (II)) and from 17.11% to 72.37% (Cu (II)). Further increase in biomass quantities did not enhance the removal efficiency. Thus, the optimum sawdust quantity for biosorption of Zn (II) and Cu (II) was found to be 5 g.

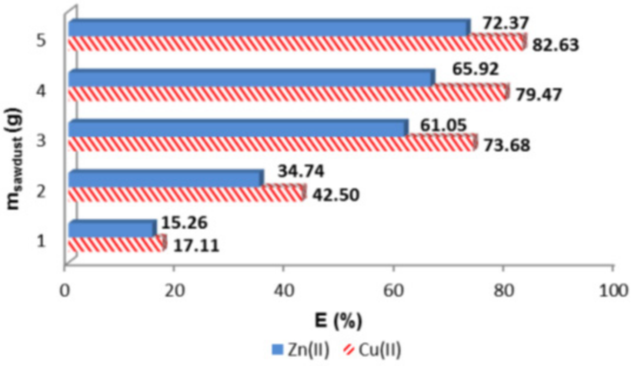

Figure 2. The effect of fir tree sawdust biomass quantity ($m_{sawdust}$) on Zn (II) and Cu (II) adsorption over the removal efficiency (E (%)); C_i = 38 mg/L, 5 g, 0.6 < d < 1.2 mm, 296 K, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

3.3. *Effect of initial pH*

Upon all parameters studied, it is well known that initial pH is the most important controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and to the fact that protons can strongly compete with adsorbate ions. In the present study, adsorption experiments were carried out by varying the initial pH of the solution in the range of 2.3 to 8.5. The relation between the initial pH of the solution and the percentage removal of Zn (II) and Cu (II) is presented in Figure 3. It should be observed that with the increase of the initial pH, the adsorption efficiency also increased up to 82% (pH = 7.4) and 83% (pH = 6.4) for the removal of Zn (II) (Figure 3a) and Cu (II) (Figure 3b), respectively. Higher pH values did not enhance the removal efficiency for Zn (II). In low pH solutions, the presence of positively charged sites on the sawdust surface may also be responsible for the low metal uptake. On the other side, at higher pH, the adsorption surface becomes less positive and therefore the electrostatic attraction between the metal ions and sawdust surface is likely to be increased.

At pH values higher than 6.4 (at the examined copper concentration) the copper ions tended to precipitate and therefore adsorption studies could not be correctly performed. Thus the optimum initial pH of the solution providing the maximum removal of Zn (II) and Cu (II) was 7.4 and 6.4, respectively.

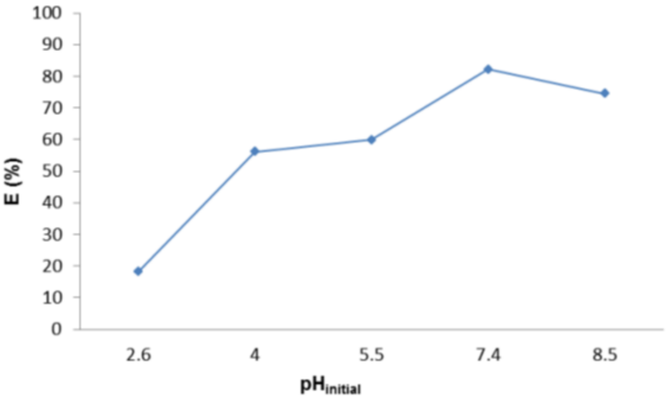

Figure 3. The effect of the initial pH values on removal efficiency (E (%)) for Zn (II) (a) and Cu (II) (b) adsorption using fir tree sawdust biomass; C_i = 48 mg/L, 5 g, 0.6 < d < 1.2 mm, 296 K and 700 rpm.

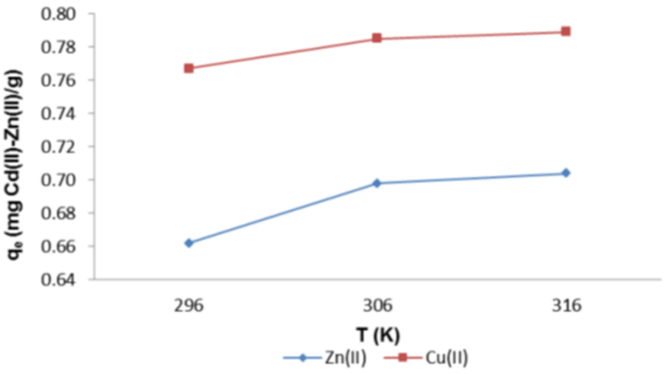

Figure 4. Temperature influence over the removal efficiency (E (%)) of Zn (II) and Cu (II) adsorption; C_i = 55 mg/L (Zn)/ 43 mg/L (Cu), 5 g, 0.6 < d < 1.2 mm, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

3.4. *Effect of temperature*

The effect of temperature on the adsorption capacity of Zn (II) and Cu (II) was studied in the range of 296 – 316 K. Results are presented in Figure 4. The adsorption of metal ions was found to increase with the rise of temperature within this range, which clearly indicates the endothermic nature of the process. The enhanced adsorption capacity may be attributed to either the change in pore size (at higher temperatures) of the adsorbent, causing intra-particle diffusion within the pores, or the chemical interaction between adsorbate and adsorbent, which creates new adsorption sites (Zakaria et al., 2009; Meena et al., 2008; Sciban et al., 2007; Argun et al., 2007).

If temperature raises even further, the thermal energy of the system increases, thereby increasing the mobility of the adsorbate causing desorption.

3.5. Effect of initial concentration and contact time

The biosorption of Zn (II) and Cu (II) was carried out at different initial ion concentrations in the range of 38 to 250 mg/L, pH 5.5 (Zn)/4.6 (Cu) contacting 5 g sawdust, at room temperature (23 °C) with 240 min of contact time (until equilibrium was reached). It was observed in experimental studies that increasing the initial concentrations of the metal ions from 38 to 250 mg/L, the amount adsorbed increased from 0.55 to 1.55 mg/g for zinc ions and from 0.59 to 2.10 mg/g for copper ions (Figure 5a). The increase in adsorption capacity may be due to the occupation of all possible and available active sites present on the adsorbent surface. Moreover, a higher initial concentration provides an important initial force to overcome the pollutant's mass transfer resistances between aqueous and solid phases. Further increase of the initial metal ion con-

Table 1. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental qe values for Zn (II) and Cu (II) adsorption on sawdust biomass using different initial concentrations; C_i = 38-250 mg/L, 5 g, 0.6 < d < 1.2 mm, 296 K, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

C (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e (calc) (mg/g)	R^2	k_2 (g/mg.min)	q_e (calc) (mg/g)	R^2
Zn (II)							
38	0.55	2.3×10^{-2}	0.205	0.948	10.18×10^{-2}	0.56	0.999
103	0.93	1.71×10^{-2}	0.451	0.944	35.10×10^{-2}	0.96	0.997
150	1.15	1.4×10^{-2}	0.573	0.893	6.38×10^{-2}	1.20	0.997
205	1.48	1.3×10^{-2}	0.579	0.919	7.51×10^{-2}	1.50	0.998
250	1.55	1.07×10^{-2}	0.712	0.919	4.67×10^{-2}	1.58	0.993
Cu (II)							
38	0.59	4.88×10^{-2}	0.209	0.722	71.90×10^{-2}	0.63	1
103	1.50	4.94×10^{-2}	0.512	0.771	33.61×10^{-2}	1.51	1
150	1.83	4.05×10^{-2}	0.627	0.706	19.94×10^{-2}	1.84	1
205	1.99	3.82×10^{-2}	0.610	0.641	19.34×10^{-2}	2.01	1
250	2.10	1.92×10^{-2}	0.868	0.464	5.05×10^{-2}	2.13	0.995

Table 2. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin coefficients calculated using linear regression analysis for Zn (II) and Cu (II) adsorption on sawdust biomass; C_i = 38-250 mg/L, 5 g, 0.6 < d < 1.2 mm, 296 K, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

Metal ions	Langmuir			Freundlich			Dubinin-Radushkevich			Temkin		
	K_L (L/mg)	q_{max} (mg/g)	R^2	n	K_f ($mg^{(1-1/n)} L^{1/n}/g$)	R^2	β ($mol^2\ kJ^2$)	E (kJ/mol)	R^2	A_T (L/g)	B (J/mol)	R^2
Zn(II)	8.32	1.46	0.939	2.66	0.220	0.980	4×10^{-9}	3.54	0.981	1.88	5×10^{-5}	0.923
Cu(II)	3.40	2.48	0.998	2.46	0.315	0.917	2×10^{-9}	5	0.922	1.94	8×10^{-5}	0.975

Table 3. Thermodynamic parameters for the adsorption of Zn (II) and Cu (II) on sawdust biomass at various temperatures; C_i = 55 mg/L (Zn)/ 43 mg/L (Cu), 5 g, 0.6 < d < 1.2 mm, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

Metal ions	Δ*S*°	Δ*H*°	Δ*G*°, (kJ/mol)		
	(kJ/K.mol)	(kJ/mol)	296 K	306 K	316 K
Zn(II)	-7.5×10^{-3}	6.36	8.58	8.66	8.73
Cu(II)	2.5×10^{-2}	11.7	4.27	4.02	3.77

centration does not raise the adsorption capacity.

The effect of contact time on Zn (II) and Cu (II) adsorption onto sawdust was investigated to study the rate of heavy metal ions removal at an initial concentration of 38 mg/L (for both metals). Figure 5b shows the percentage of heavy metal ions adsorbed as a function of contact time. It is evident that the adsorption process achieved the maximum removal efficiency of 65% (Zn (II)) and 75% (Cu (II)) almost in the first 60 min of contact. The higher removal efficiency in this time range is due to the fact that at the beginning of the experiment a larger surface area of sawdust was available for metal adsorption. The final equilibrium was reached after 240 min. A longer contact time had no effect on the adsorption. Our results were in concordance with the scientific literature. Blázquez et al. (2012) found out that equilibrium was reached between 60 and 100 min during copper biosorption by pine cone shell; whereas Ho (2003) indicated that the equilibrium time for biosorption of copper using tree fern was less than 60 min. Kapur and Mondal (2013) indicated that the time needed to reach equilibrium during Cr(VI) adsorption by *Mangifera indica* sawdust was around 60 min. Further increase in the contact time has an insignificant effect on the rate of adsorption.

3.6. Adsorption kinetics

The kinetics of adsorption was studied in order to evaluate the adsorption dynamics and the process time required to achieve equilibrium between the aqueous and the solid phases. To analyze the adsorption kinetics of Zn (II) and Cu (II) ions onto sawdust, experimental data were tested with the most widely used Lagergren's pseudo-first-order and Ho's and McKay pseudo-second-order models. The values of k_1 and R^2 along with the calculated uptake capacity $q_{e(calc)}$, are provided in Table 1. As the table shows, low correlation coefficients values were obtained for both metal ions studied (in range of 0.8933-0.9476 and 0.4638-0.771 for Zn and Cu, respectively). Also, the calculated uptake capacities of adsorption equilibrium were much lower than the experimental uptake capacity $q_{e(exp)}$ values. Therefore, it can be concluded that the Lagergren pseudo-first-order model is not suitable to describe the heavy metal adsorption on sawdust. By plotting the t/q_t versus t, the rate constant k_2, the calculated uptake capacity $q_{e(calc)}$ and the correlation constant R^2 were calculated and summarized in Table 1. The calculated uptake capacity values agree very well with the experimental values and the R^2 values also exceed 0.993. This indicates the applicability of the Ho and McKay pseudo-second-order model for describing the adsorption of Zn (II) and Cu (II) onto the selected adsorbent.

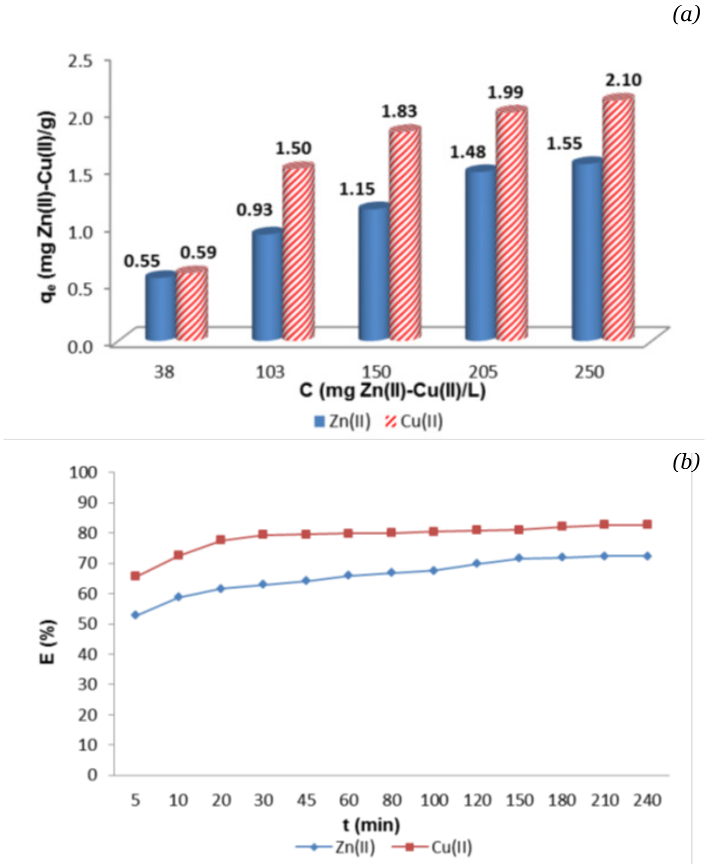

Figure 5. Influence of the initial Zn (II) and Cu (II) concentration over the (a) adsorption capacity (q_e) and (b) time evolution over the removal efficiency (E (%)) on fir tree sawdust biomass; (a) C_i = 38-250 mg/L; (b) C_i = 38 mg/L, 5 g, 0.6 < d < 1.2 mm, 296 K, 5.5 (Zn)/4.6 (Cu) pH and 700 rpm.

3.7. Adsorption isotherms

Analysis of equilibrium data is important to determine the adsorption mechanism and adsorption capacity. Therefore the most widely known adsorption models, such as the Langmuir Freundlich, Dubinin-Radushkevich (D–R) and Temkin models, were used to describe the equilibrium established between the adsorbed metal ions (q_e) and the metal ions remaining in the solution (C_e), under predefined conditions of pH, initial metal ion concentrations, temperature, biomass quantity, particle size and stirring rate.

The values of q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e

versus C_e/q_e. The values of the Langmuir parameters (Table 2), q_{max} and K_L, were 1.46 (mg/g) and 8.32 (L/mg); and 2.48 (mg/g) and 3.40 (L/mg) for the Zn (II) and Cu (II), respectively. The correlation coefficient R^2 was found to be 0.940 and 0.998 for the Zn (II) and Cu (II), respectively (Table 2). Maximum adsorption capacities obtained for different types of sawdust for the removal of Zn (II) and Cu (II) from aqueous solutions have been reported in literature. Li et al. (2007) report that the maximum adsorption capacity of poplar tree sawdust for the removal of Cu(II) was 6.58 mg/g (Li et al., 2007). Another study shows that sawdust obtained from deciduous trees presents relative high adsorption capacity on the removal of zinc (2.17 mg/g) and copper (9.9 mg/g) ions from aqueous solutions (Božić et al., 2009).

The Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$ on the basis of the linear form of the Freundlich equation, presented in Table 2. The values of n and K_F were 2.66 and 0.220 for Zn (II) and 2.46 and 0.315 for Cu (II), respectively. The value of n, which is related to the distribution of bonded ions on the adsorbent surface, represents beneficial adsorption if it is between 1 and 10 (Ibrahim et al., 2006; Chakravarty and Sarma, 2010). The n value for the used biosorbent was found to be greater than one, indicating that adsorption of Zn (II) and Cu (II) was favorable. The correlation coefficients R^2 were found to be 0.980 and 0.917 for Zn (II) and Cu (II) respectively (Table 2). Comparing the correlation coefficients, the obtained results indicate that the equilibrium data in case of Zn (II) removal fitted well with the Freundlich isotherm model, while the Cu (II) removal was more appropriately described by the Langmuir isotherm model.

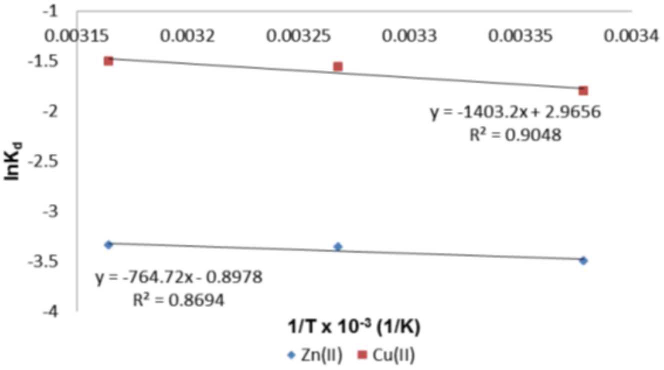

Figure 6. Plot of $\ln K_d$ versus 1/T for the estimation of the thermodynamic parameters for Zn (II) and Cu (II) adsorption on fir tree sawdust biomass.

The D–R isotherm constant shown in Table 2 can be calculated from the intercept of the plot between $\ln q_e$ and ε^2. The magnitude of the mean free energy of adsorption (E) provides information on the nature of the adsorption process, i.e. whether it is physical or chemical. The E values in the range of 1 and 8 kJ/mol correspond to physical sorption and in the range of 9 and 16 kJ/mol to chemisorption (Jain et al., 2009). In our study, the calculated E value was found to be 3.54 and 5 for Zn(II) and Cu(II) respectively, indicating a physisorption process.

The obtained constants from the plots between q_e versus $\ln C_e$ for the Temkin model are given in Table 2. The good fitting of the value of R^2 does not contradict the applicability of the linear model that suggests the abundance of sites having an equal affinity for adsorption (Mahajan and Sud, 2013).

3.8. Thermodynamic parameters

In order to demonstrate the nature of adsorption of Zn (II) and Cu (II) onto sawdust, thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{11}$$

$$\Delta G^\circ = -RT \ln K_d \tag{12}$$

where K_d is the equilibrium constant at temperature T and R the universal gas constant. Thermodynamic parameters can be determined using the equilibrium constant, K_d (q_e/C_e), which depends on temperature. Experimental results were used to calculate the thermodynamic parameters and are presented in Figure 6 and Table 3. The overall adsorption process for both metals studied was determined to be an endothermic one (positive values of ΔH° = 6.36 and 11.67 kJ/mol for Zn (II) and Cu (II), respectively). Positive small values of free energy indicate that the considered adsorption process will be promoted by specific temperature conditions, leading to increased adsorption capacities (Nagy et al., 2013). The negative value obtained for ΔS° in case of Zn (II) adsorption refers to decrease in the degree of freedom due to the association of adsorbate species on the sawdust particles (Kapur and Mondal, 2013). Beside this, positive values of entropy were calculated in case of Cu (II) adsorption, which point to some structural changes as a result of the interaction of copper ions with the active sites of sawdust (Ahmad et al., 2007).

4. CONCLUSIONS

Here we presented the results of adsorption studies using a wood-industrial waste material, sawdust, as adsorbent for the removal of Zn (II) and Cu (II) ions from synthetic aqueous single metal solutions. FTIR analysis indicated the presence of hydroxyl, amino and carboxyl groups on the adsorbent surface which play an important role in the adsorption process. We also showed that the adsorption capacity increased with the increase of initial metal ion concentration, contact time and biomass quantity up to a certain level. Maximum zinc and copper removal was observed at the initial pH of 7.4 and 6.4, respectively. The adsorption equilibrium was reached rapidly, after around 60 min of contact time. This equilibrium was also characterized by kinetic and isotherm studies. The kinetic studies concluded that the pseudo-second-order model fits better both studied metal ions. The equilibrium adsorption data were tested with four isotherm models, namely Langmuir, Freundlich, Dubinin-Radushkevich (D–R) and Temkin. The equilibrium data in case of Zn (II) adsorption was best described with the Freundlich isotherm model, while the Cu (II) removal fits well with the Langmuir isotherm model. According to the Dubinin-Radushkevich model, the adsorption of the studied heavy metals was physical in nature. After evaluating the thermodynamic parameters (positive values of ΔH°), it can be concluded that the adsorption of Zn (II) and Cu (II) onto sawdust was of endothermic nature.

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