ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim., **2015**, *60*(2-3), 257-264

Dedicated to Professor Zeno Simon on the occasion of his 80th anniversary

ISOTHERM AND THERMODYNAMIC STUDIES OF Cd (II) REMOVAL PROCESS USING CHEMICALLY MODIFIED LIGNOCELLULOSIC ADSORBENT

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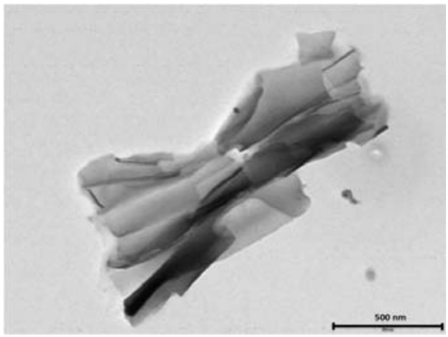
Received July 17, 2014

The present study gives important information about Cd (II) removal process from synthetic aqueous solutions using modified (NaOH and H_2O_2) industrial residue, Romanian fir tree sawdust as adsorbent. Batch experiments were carried out to investigate the effect of stirring rate, biomass quantity and contact time. The changes in morphological structure after the chemical treatment were evaluated by TEM analysis. Isotherm models (Dubinin-Radushkevich and Temkin) and thermodynamic parameters of the considered adsorption process were discussed in details. Our results showed that the adsorption process for the two types of treatment, revealed different thermodynamic behaviour. The adsorption data of Cd (II) ions were fitted well on Dubinin-Radushkevich and Temkin isotherm models. The findings of the investigation suggested that the physical adsorption was controlling the adsorption rate.



INTRODUCTION

The global industrialization and the various chemical compounds production development have led to serious deterioration of the environment quality. Heavy metals are between the most toxic pollutants for natural waters because of their long persistence in the environment.[1]

The main industrial sources of heavy metal pollution are: metallurgy, mining, textile industry, paint pigments, metal plating etc.[2]

Conventional methods, such as chemical precipitation, chemical oxidation and reduction, filtration, ion exchange, membrane processing etc., have been traditionally employed for heavy metals removal from industrial wastewaters.[3] The majority of these techniques have limitations, for example are less effective and require several pre-treatments involving high capital cost.[4] The biosorption has distinct advantages over these conventional methods as it is non-polluting and can be highly selective, easy to operate and more efficient from the technological and economical point of view.[5]

The use of low-cost adsorbents has been investigated as a replacement for costly current methods. Interest has arisen recently in removing

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heavy metals from solution by binding with agricultural cellulosic wastes such as nut wastes, tree barks, cotton and sawdust. Many agricultural and industrial by-products have small or no economic value and some, such as short fibres from jute waste processing and sawdust, which are produced in large quantities often, present a disposal problem. If these by-products could be used as adsorbents, contaminated water streams would be cleaned and a new market would be opened for these by-products.[6]

Sawdust obtained from wood industry is an abundant by-product which contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that could bind Cd (II) ions through different mechanisms.

Cellulose is the most common polysaccharide consisting of a linear chain of hundreds to thousends of β-(1-4) linked D-glucose units.[7] Hemicellulose is a complex carbohydrate structure that consists of different polymers like pentoses (xylose and arabinose), hexoses (like mannose, glucose and galactose) and sugar acids. The dominant component of hemicellulose from hardwood and agricultural plant, like grasses and straw, is xylan, while for softwood this is glucomannan.[8] Lignin is, after cellulose and hemicellulose, one of the most abundant polymers in nature and is present in the cellular wall. It is an amorphous heteropolymer consisting of three different phenylpropane units (*p*-coumaryl, coniferyl and sinapyl alcohol) that are held together by different kind of linkages. The main purpose of lignin is to give the plant structural support, impermeability and resistance against microbial attack and oxidative stress.[9]

The aim of this work was to study the thermodynamic aspects and the adsorption process of Cd (II) on NaOH and H_2O_2 treated fir tree sawdust. Equilibrium data were modelled using Dubinin-Radushkevich and Temkin isotherms. The effect of stirring rate, biomass quantity and contact time were investigated. TEM microscope images were used for surface morphology characterization of the studied biomass.

RESULTS AND DISCUSSION

TEM analysis

The transmission electron micrographs enable the direct observation of the surface morphological structure of different adsorbents. TEM studies (Fig. 1) of the untreated (raw) and NaOH treated fir tree sawdust were conducted in order to understand the role of this structure in the Cd (II) binding mechanisms. As Fig. 1a shows, the surface morphology of untreated sawdust presents a regular, rough, heterogeneous layered structure aggregated in small lamellar domains with parallel orientation. After NaOH treatment, deformation of the regular pattern and some distortion of the shape could be observed, Fig. 1b. These surface structure modifications could justify the enhancement of Cd (II) binding onto NaOH treated fir tree sawdust.

Effect of contact time

In order to establish the evolution in time of Cd (II) adsorption on treated fir tree sawdust, cadmium concentration was investigated as a function of contact time and the results are presented in Fig. 2.

It can be observed that the adsorption rate increase rapidly at the begining (less than 100 min) due to the abundant availability of active binding sites on the adsorbent, while with gradual occupancy of these sites, the adsorption became less efficient towards the later stages. Further increase in contact time did not enhance the adsorption, therefore the contact time was selected to be 240 min for further experiments (equilibrium). The mechanism of solute transfer to the adsorbent surface includes diffusion through the thin film surrounding the solid particle and diffusion through the pores to the internal adsorption sites.[10]

Effect of stirring rate

The effect of stirring rate is an important parameter which affects the adsorption capacity and removal efficiency, therefore, an optimal speed should be used in wastewater treatment.[11] Stirring rates ranging between 100 and 700 rpm were tested. As Fig. 3 shows, the maximum removal efficiencies for both treated fir tree sawdust were were obtained at 700 rpm, 98% and 96% for NaOH and H_2O_2, respectively.

An increase in stirring rate reduced the film boundary layer surrounding the adsorbent particles, thus, increasing the external film mass transfer coefficient and hence, the rate of uptake. Therefore, a stirring speed of 700 rpm was selected for further experiments.

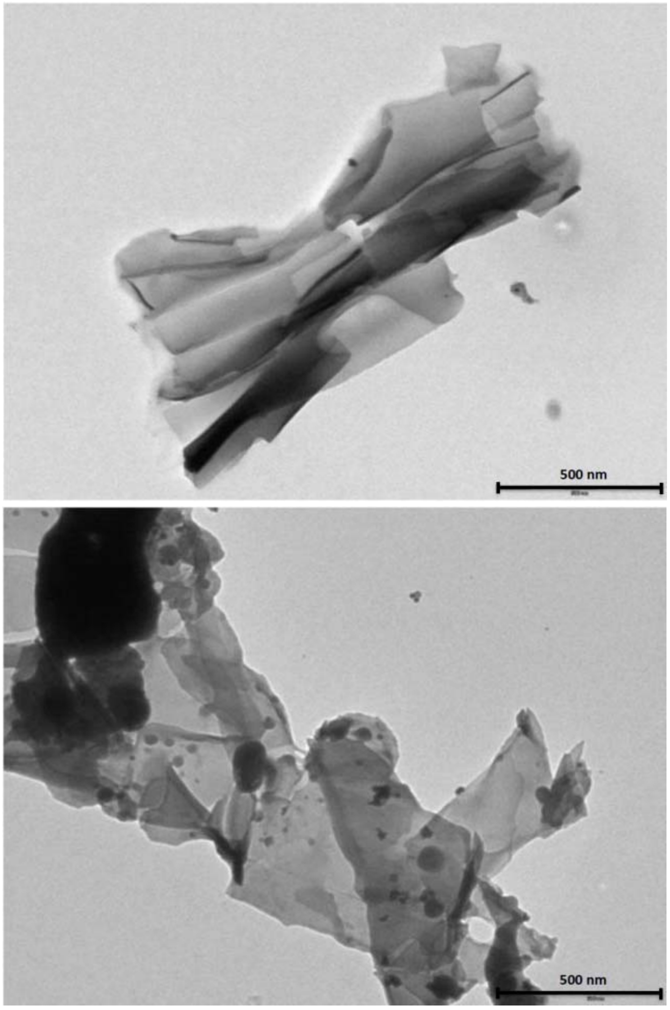

Fig. 1 – TEM images of (a) untreated (8000×) and (b) NaOH (8000×) treated fir tree sawdust.

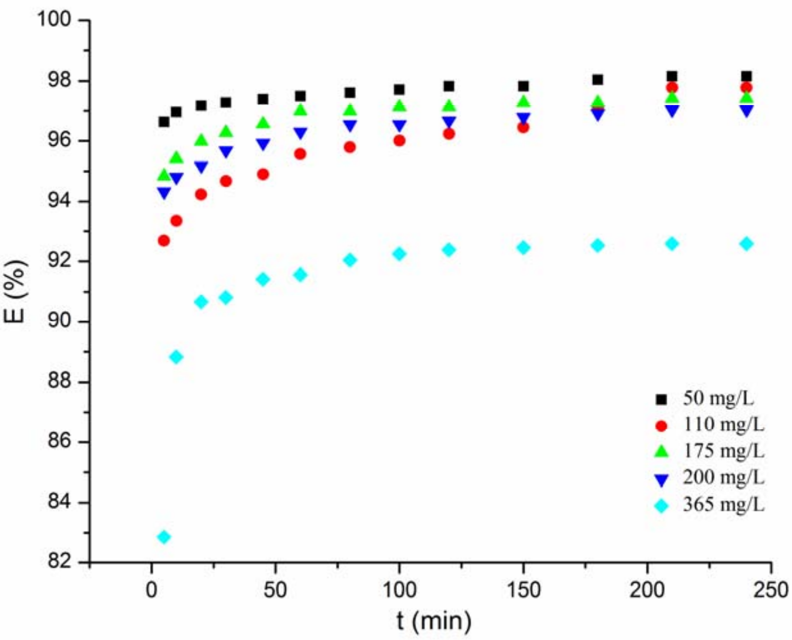

Fig. 2 – The effect of contact time over the removal efficiency for Cd (II) adsorbtion on NaOH treated fir tree sawdust on Cd (II) adsorption; C_i = 50-365 mg/L, 5 g biomass, d = 0.4-0.6 mm, 296 K, pH 5.5, 700 rpm.

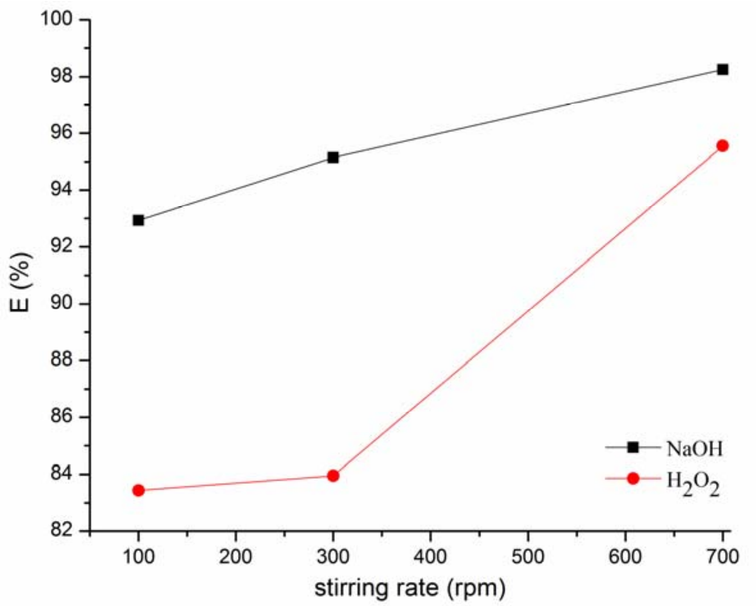

Fig. 3 – The effect of stirring rate over the removal efficiency for Cd (II) treated fir tree sawdust on Cd (II) adsorption; C_i = 50 mg/L, 5 g biomass, d = 0.4-0.6 mm, 296 K, pH 5.5.

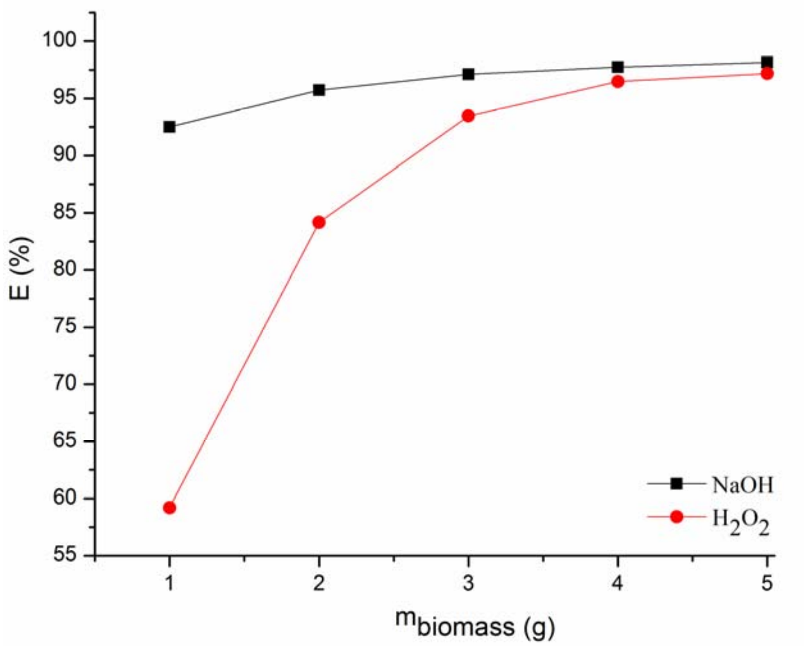

Fig. 4 – The effect of the biomass quantity on Cd (II) removal efficiently; C_i = 50 mg/L, d = 0.4-0.6 mm, 296 K, pH 5.5, 700 rpm.

The effect of biomass quantity

The study of chemically treated fir tree sawdust quantity effect over Cd (II) removal were realized at room temperature with an initial concentration of 50 mg/L Cd (II), varying the quantity of adsorbent from 1 to 5 g.

The effect of the treated fir tree sawdust quantity on the adsorption efficiency of Cd (II) is presented in Fig. 4. The removal efficiencies increase with an increase in the adsorbent quantity.

This trend can be attributed to a higher surface area and availability of more adsorption sites. The maximum removal efficiencies reached values of 98% and 97% for NaOH and H_2O_2, respectively, as biomass quantity biomass quantity reached 5 g. In case of untreated fir tree sawdust, maximum removal efficiency value was 83% (experiments were carried out in the same conditions).[12] Further increase of the adsorbent quantity did not lead to an increase in removal efficiency values, therefore, subsequent experiments were conducted using 5 g of biomass. These results also showed that the chemical treatment of sawdust significantly enhanced the adsorption performance of the natural (raw) adsorbent.

Adsorption isotherm models

Equilibrium adsorption isotherms have fundamental importance for adsorption processes design since they indicate how metal ions are partitioned between the adsorbent surface and liquid phases at equilibrium as a function of metal concentration.[11] In order to characterized the mechanisms for the interaction of Cd (II) with the biosorbent site, beside Langmuir and Freundlich isotherms,[12] Dubinin-Radushkevich and Temkin adsorption isotherm models were selected to be studied.

The Dubinin-Radushkevich model was applied to the equilibrium data to determine if adsorption had occurred by physical or chemical processes.[13] The Dubinin-Radushkevich adsorption isotherm can be expressed as:[14]

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad (1)$$

where, q_m is the theoretical adsorption capacity (mg/g), β is Dubinin-Radushkevich model constant ($mol^2\ kJ^2$), ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \qquad (2)$$

where, R is the universal gas constant (8.314 J/ mol K) and T is the absolute temperature (K).

Free energy E per molecule, of adsorbate, which helps to distinguish between the physical and chemical adsorption of metal ions is given below:

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (3)$$

The isotherm constants q_m and β were obtained from the intercept and the slope of the plot $\ln q_e$ *vs.* ε^2.

If E value is between 8 and 16 kJ/mol, the adsorption adsorbtion follows an ion-exchange and if E < 8 kJ/mol, the adsorption process is physical.[15] In our case, for the NaOH and H_2O_2 treated fir tree sawdust the mean free energy was 3.16 and 5 kJ/mol (Table 1), respectively, which corresponds to physical adsorption.

Temkin isotherm equation contains a factor that takes into account the adsorbent-adsorbate interactions.[16] It is based on the fact that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate-adsorbent repulsions and the adsorption of cadmium ions uniformly realised on the surface.[17,18] In addition, it also assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich isotherm. The equation of this model is given below:

$$q_e = B\ln A_t + B\ln C_e \qquad (4)$$

$$B = \frac{RT}{b_T} \qquad (5)$$

where, T is the absolute temperature in Kelvin and R is the universal gas constant, A_T is the Temkin isotherm equilibrium constant (L/g), b_T is Temkin isotherm constant and B is a constant related to the heat of adsorption (J/mol). From the q_e *vs.* $\ln C_e$ plot, A_T and B constants were determined.

Table 1

Dubinin-Radushkevich and Temkin constants for Cd (II) adsorption on fir tree treated sawdust biomass; C_i = 50-365 mg/L, 5 g biomass, d = 0.4-0.6 mm, 296 K, pH 5.5, 700 rpm

	Dubinin-Radushkevich			**Temkin**		
	β ($mol^2\ kJ^2$)	**E (kJ/mol)**	**R^2**	**A_T (L/g)**	**B (J/mol)**	**R^2**
NaOH	5×10^{-9}	3.16	0.9689	2.33	2×10^{-4}	0.9898
H_2O_2	2×10^{-9}	5	0.9497	2.17	4×10^{-5}	0.9749

Atkins, 1999 revealed that, if the mean free energy and heat of adsorption values (kJ/mol) are lower than 20 kJ/mol, physisorption process can occur.[19] Taking into consideration the calculated value of the constant related to heat of sorption, which has a value smaller than 20 kJ/mol (Table 1), we concluded that according to this isotherm the adsorption process takes place as physisorption.

Thermodynamic parameters

The temperature dependence for Cd (II) ions adsorption on treated fir tree sawdust was evaluated using the following equations:[20]

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

where ΔH°, ΔS°, ΔG°, and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature 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 (Table 2).

Experimental results were used to calculate the thermodynamics parameters and are presented in Fig. 5 and Table 3. The two treatments showed different thermodynamic behaviour.

For the NaOH treatment, negative value of ΔH° indicates that the adsorption process is exothermic in nature. Also, a small negative value of entropy suggests the probability of favourable adsorption and also the disorder degree of the adsorption at solid-liquid interface.[21] Small negative to small positive values with the increase of temperature were obtained for ΔG°, indicating the spontaneous nature of the adsorption process.

In case of H_2O_2 treatment, positive value of ΔH° (19.87 kJ/mol) and small positive to small negative values of ΔG° were calculated, which showed that the overall process is endothermic. This occurs as a result of redistribution of energy between the adsorbate and adsorbent. Before adsorption occurs, cadmium ions near the surface of the treated fir tree sawdust will be more ordered than in the subsequent adsorbed state and the ratio of free cadmium ions to ions interacting with the adsorbent will be higher than in the adsorbed state.[10]

Table 2

Adsorption capacity and equilibrium concetration values for the adsorption of Cd (II) on fir tree treated sawdust at various temperatures; C_i = 50 mg/L, 5g biomass, d = 0.4-0.6 mm, pH 5.5, 700 rpm

Treatment	**T (K)**	**q_e (mg/g)**	**C_e (mg/L)**
NaOH	296	0.949	0.85
	306	0.947	0.95
	316	0.944	1.10
H_2O_2	296	0.965	1.40
	306	0.972	1.05
	316	0.976	0.85

Table 3

Thermodynamic parameters for the adsorption of Cd (II) on fir tree treated sawdust at various temperatures; C_i = 50 mg/L, 5g biomass, d = 0.4-0.6 mm, pH 5.5, 296-316 K, 700 rpm

Treatment	**T (K)**	**ln K_d (q_e/C_e)**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (kJ/K·mol)**
NaOH	296	0.110	-0.15	-10.21	-3.41×10^{-3}
	306	-0.003	0.19		
	316	-0.153	0.53		
H_2O_2	296	-0.372	0.93	19.87	6.43×10^{-3}
	306	-0.077	0.29		
	316	0.138	-0.35		

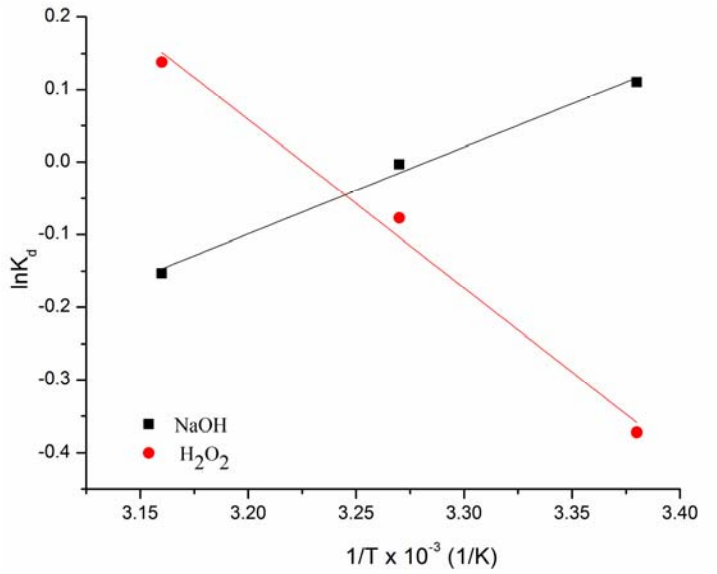

Fig. 5 – Plot of $\ln K_d$ versus 1/T for the estimation of the thermodynamic parameters for Cd (II) adsorption on fir tree treated sawdust.

The kinetics of the considered adsorption process was reported previously and was found that Cd (II) adsorption on chemically treated fir tree sawdust obeyed the pseudo-second-order kinetic model.[22] Therefore, taking in account that generally the rate of reaction is temperature dependent, using pseudo-second-order rate constant determined at minimum three temperatures it is possible to calculate the activation energy of the adsorption process using Arrhenius equation:[23]

$$k = A \cdot e^{\frac{-Ea}{RT}} \quad (8)$$

where, k is rate constant for pollutant removal (second order) (g/min), A is Arrhenius constant (g/min), R is the universal gas constant and T is the absolute temperature (K).

Activation energy can be calculated from linear plot lnk *vs*. 1/T.

$$\ln k = \ln A - \frac{Ea}{RT} \quad (9)$$

The calculated E_a values were found to be 31.2 and 25.56 kJ/mol for NaOH and H_2O_2, respectively. Film diffusion typically has activation energy of 17-21 kJ/mol and pore diffusion has activation energy of 21-42 kJ/mol.[24] Thus, the E_a values showed that the adsorption of Cd (II) on chemically treated sawdust is pore-diffusion controlled. The activation energy value also gives us information on whether the adsorption is mainly physical or chemical: physisorption process normally has activation energy of 5-40 kJ/mol, while chemisorption has higher activation energy (40-800 kJ/mol).[25] In our case, the E_a values obtained for Cd (II) removal for both treatments lie in the range of physical adsorption.

EXPERIMENTAL

Adsorbent

The fir tree (*Abies alba*) sawdust was obtained from a local sawmill in Huedin, Cluj County, Roumania. Prior to its utilization the considered biomass 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 grinded and sieved (400-600 µm). The sieved sawdust was then stored in an airtight box before its utilization.

Fir tree sawdust was modified using NaOH (1%) and H_2O_2 (1M) solutions.[22,26,27]

Metal solution

The stock solution, 1 g/L of Cd (II), was prepared by dissolving $Cd(NO_3)_2 \times 4H_2O$ in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in 50-365 mg/L range. All chemicals used were of analytical grade.

Microscopy investigations

Transmission electron microscopy (TEM) for the untreated and NaOH treated adsorbent were performed using a Hitachi Automatic TEM H7650 equipment (accelerating voltage 40-120 kV, zoom 200x-600000x) by dipping a holey-carbon TEM grid into a suspension of biomass. Samples were imaged using an Olympus KeenView G2 camera, transmission electron microscope operating at 120 kV.

Batch adsorption studies

The adsorption of Cd (II) on treated fir tree sawdust was studied using batch technique. Experiments were carried out by contacting 1-5 g of treated biosorbent at different stirring rates (100-300-700 rpm) and 23ºC with 100 mL Cd (II) ions in aqueous solutions. In order to establish the evolution of the removal process (with different initial concentrations in range of 50-365 mg/L), 100 µL samples were collected at different time intervals up to 240 minutes (preliminary experiments showed that this time is sufficient for attaining the equilibrium). Samples collected at predetermined time intervals were filtered (ME cellulose 0.45 µm microfilter) and the remaining concentration in aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia).

The evaluation of Cd (II) uptake at equilibrium for the treated fir tree sawdust samples was realised using adsorption capacity, q_e (mg/g) and removal efficiency, E (%) values. Other adsorption parameters of chemically treated fir tree sawdust was studied in detail and reported.[22]

All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

CONCLUSIONS

The adsorption study performed presents the utilization of chemically modified waste material, fir tree sawdust, for Cd (II) removal process from synthetic aqueous solutions.

Operational parameters such as stirring rate, adsorbent quantity, and contact time clearly affected the removal process. With an increase in biomass quantity, removal efficiencies increased up to 98% for both types of treatments. The removal process showed that the adsorption rate of Cd (II) is faster for the initial 80-100 min and then it decreases in the later part of adsorption towards equilibrium (240 min). Equilibrium (Dubinin-Radushkevich and Temkin) isotherms and thermodynamics of the considered adsorption process were discussed in details. According to the two isotherm models the adsorbtion of Cd (II) on fir tree sawdust was physical in nature.

Thermodynamics parameter values indicate that the adsorption process is spontaneous for both treatments, it has an exothermic nature in case of NaOH treatment and an endothermic nature for the H_2O_2 treatment.

The activation energy values showed that Cd (II) was mainly adsorbed physically onto NaOH and H_2O_2 treated fir tree sawdust, confirming the results obtained using the two isotherm models.

Based on the obtained results, it can be concluded that the chemically treated fir tree sawdust is an effective, green and alternative adsorbent for the removal of Cd (II) from aqueous solutions.

Acknowledgments: This work was possible due to the financial support of the Sectorial Operational Program for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/159/1.5/S/132400 with the title "Young successful researchers – professional development in an international and interdisciplinary environment".

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