KINETIC AND THERMODYNAMIC PROFILE OF Pb(II) SORPTION BY UNTREATED HEMP FIBERS

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Abstract

The use of low cost sorbents for removing heavy metals from wastewaters has emerged as a potential alternative method to conventional techniques (chemical precipitation, reverse osmosis, electrolysis, ion exchange). However, the success of this approach depends on economic feasibility, which can be obtained by the optimization of the environmental conditions. The results showed that sorption kinetics of Pb(II) on untreated hemp fibers could be described by pseudo –first order and pseudo – second order models. In order to evaluate the thermodynamic feasibility of the Pb (II) sorption process on hemp, the thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated At all working temperatures, the ΔG values are negative, showing the spontaneous nature a of Pb (II) sorption on hemp fibers. The positive values of ΔH indicate that the Pb (II) sorption on hemp is an endothermic process, favored by temperature increasing. For ΔS a positive value has been obtained, suggesting an increased randomness at the interface of hemp – solution and affinity of the natural hemp for Pb(II) ions.

Key words: hemp, kinetic, lead, sorption.

Heavy metals such as lead can often be found in industrial wastewaters and their discharge to the environment poses serious threat due to their acute toxicity to aquatic and terrestrial life which includes humans.

Due to the toxicological profile of lead and its persistence in environment, suitable methods are necessary for lead removal from wastewaters and drinking water sources. The contaminated effluents treatment is a process that is sometimes more complicated that any other manufacturing process, because waters can have a very variable composition in terms of organic or inorganic compounds, extreme acidity or basicity, presence of volatile substances or so on. Therefore, few processes provide clean effluents while fulfilling at the same time, requirements such as economic costs, flexibility in terms of both the amount of effluent to be treated and the pollutant concentration present, continuity of the system, minimal supervision and maintenance and sufficient selectivity regarding the removal of the metal considered. In this sense, sorption on low cost sorbents has been proposed as one of the most promising technologies for the removal of toxic metals from wastewaters (Bailey, S.E. et.al., 1999; Kumar, U,. 2006; Igwa, J,C, Abia, A.A,, 2006; Hlihor, R.M, Gavrilescu, M. 2009).

A considerable number of natural materials that are available in large quantities or certain wastes from agricultural operations have been cited in the literature for their capacity to remove lead from aqueos solutions.These comprise rice husks, maize cobs(Abdel–Ghani, N.T., 2007), wheat bran (Bulut,Y.,2006), sulphuric acid–treated wheat bran (Ozer, A.,2007), maize waste, maize leaf (Aderola Babarinde, 2006), pomergranate peel (El–Ashtoukhy,E–S.Z,2008), pecan nut shells (Vaghetti, J.C.P., 2009).

A previous study has been conducted on the potential of natural hemp fibers for the removal of lead from aqueous solutions The study found that unconventional tested material exhibits a high affinity toward the Pb(II)ions. In order to establish the optimum conditions of lead ions sorption on untreated hemp, the influence of some relevant experimental conditions (initial solution pH, metal ion concentration, sorbent dose) was studied at room temperature. To gain further insight into the potential of hemp fibers as lead(II) sorbent, a kinetic and thermodynamic study have been performed.

MATERIAL AND METHOD

Stock solutions of 2190 mg/L were prepared by dissolution of $Pb(NO_3)_2$ and standardized gravimetrically. Working solutions of Pb(II) were prepared by appropiate dilutions of stock solutions.
The kinetic and thermodynamic studies were carried out in batch sorption experiments, according to the procedure presented in *(fig. 1)*.
A GBS Avanta 2007 Atomic Absorption Spectrometer and accessories auto sampler and furnace system has been used.

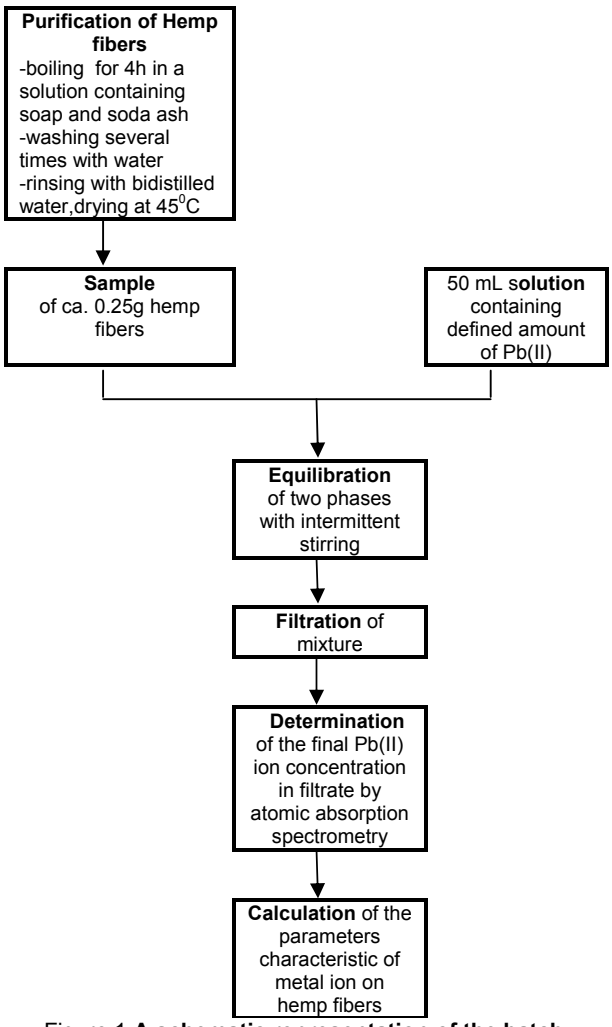

Figure 1 **A schematic representation of the batch sorption procedure carried out in this study**

RESULTS AND DISCUSSIONS

Pb(II)sorption kinetics

The kinetic of sorption, describing the Pb(II) sorption rate is an important characteristic for efficiency of sorption assessment. The kinetic data are shown in *(fig. 2).*

The kinetic curve in *(fig. 2)* shows that in the initial stages of the sorption process the amounts of Pb(II) sorbed on hemp fibers increase sharply with increasing contact time of phases, attaining values that stay almost constant.

The pseudo–first–order and pseudo–second–order rate equations were used to test the experimental data. The pseudo–first–order rate expression is given by Lagergren equation (Lagergren, S., 1898):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t$$

where q_e and q_t are the amounts of cation (mg/g) sorbed at equilibrium and at time t, respectively and k_1 is the pseudo-first order sorption rate constant(min^{-1}). The kinetic parameters obtained from the linear Lagergren plots are given in *(tab.1),* together with the corresponding correlation coefficient(R^2)

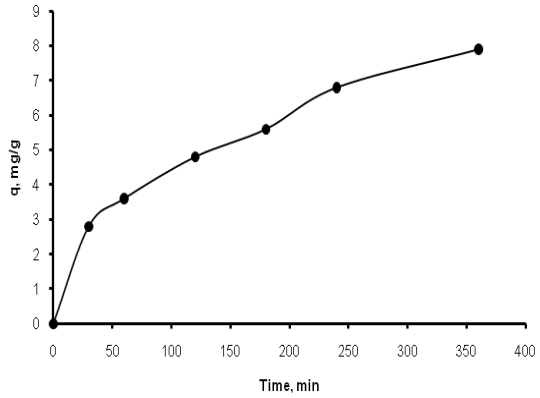

Figure 2 **The influence of contact time on the Pb(II) sorption from solutions with different initial concentrations(C_0) by the tested fly ash**

The pseudo–second–order kinetic model is based on following equation (Ho, Y.S. 1999):

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} \cdot t$$

where $h = k_2 \cdot q_e^2$ (mg/g.min) can be regarded as initial sorption rate constant of the pseudo–second–order sorption ($g.mg^{-1} \cdot min^{-1}$). The kinetic parameters derived from the plot of the liniarized form of the pseudo–second–order equation are recorded in *(tab. 1),* along with the corresponding correlation coefficient.

Table 1

Pseudo – first order and pseudo – second - order kinetic model parameters for Pb(II) sorption on natural hemp fibers at pH= 4.5 – 5 and t=20^{0}C

Pseudo-first order		Pseudo-second order			
K_1 ($.min^{-1}$)	R^2	K_2 / mg.min	h mg/g.min	q_e mg/g	R^2
$2.53x10^{-3}$	0.9913	$8,84x10^{-4}$	0.0859	9.68	0.9344

As can be seen from (*tab.1)*, the plot for the pseudo–first–order model yields better value of the correlation coefficient as compared with the plot of pseudo–second–order. This fact suggests that the Pb(II) ions on the untreated hemp follows better the pseudo–first -order kinetic model.

Pb(II) sorption isotherms

In order to successfully represent the dynamic sorptive behaviour, it is important to have a satisfactory description of the equilibrium state between the two phases composing the sorption system. The Langmuir sorption isotherm model was tested to fit the experimental data.

The Langmuir sorption isotherm is given by equation(Langmuir, I, 1916):

$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$ where K_L is a constant related to the sorption capacity and q_0 is the maximum capacity of sorption. The Langmuir equation assumes the formation of a monolayer coverage of Pb(II) at the ash surface containing a finite number of homogeneous sites of sorption. The Langmuir isotherms for Pb(II) on untreated hemp fibers at different temperatures are presented in *(fig. 3).*

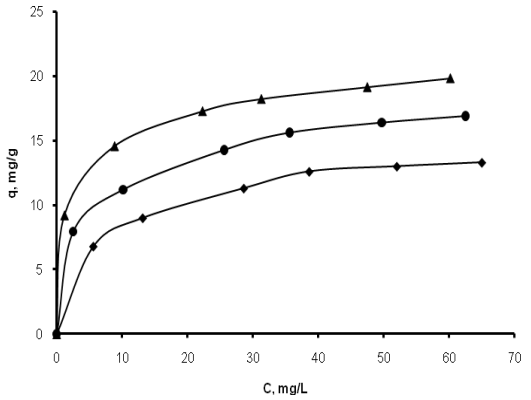

Figure 3 **Langmuir isotherms for Pb(II) sorption on hemp at: (♦) 4^{0}C; (●) 25^{0}C; (▲) 60^{0}C**

Table 2 characterizes the Pb(II) sorption on natural hemp under study by means of Langmuir constants obtained from the corresponding linear Langmuir plots.

Table 2

Quantitative description of the sorption system Pb(II) – natural hemp fibers on the basis of Langmuir model

T, K	Langmuir isotherm		
	q (mmol/g)	K_L (L/mol)	R^2
277	0.100	6164.8	0.9865
298	0.121	7353.3	0.9932
333	0.137	9365.24	0.9933

It can be seen from (*tab. 2)* that the unconventional material under study may be considered as a reasonable sorbent for Pb(II)ions removal from aqueous solutions. It was found that the low values for q_0 reported in *(tab. 2)* are in good agreement with literature data.

It is obvious from *(fig.3)* that the temperature has a favorable effect within the sorption system under study. Langmuir constants *(tab.2)* increase with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. Furthermore this trend indicates the endothermic and chemical nature of the studied cation sorption on natural hemp fibers.

Thermodynamics of Pb(II) sorption

In order to evaluate the thermodynamic feasibility of the Pb(II) sorption process and to confirm its nature,the thermodynamic parameters, the free energy change (ΔG), enthalpy change(ΔH) and entropy change (ΔS) have been calculated. Based on the values of the Langmuir sorption constant K_L at different temperatures, the following equations have been used(Tofan, L., 2008) :

$$\Delta G = - RT \ln K_L \qquad \ln K_L = \text{constant} = -\frac{\Delta H}{RT}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

where R is the gas constant and T is the absolute temperature. The obtained data are presented in *(tab.3).* The negative values of ΔG at all working temperature validate the feasibiliy of the sorption process and the spontaneity of the Pb(II) retention by hemp. The positive value of ΔH shows the endothermic nature of the Pb(II) sorption process, favored by temperature increasing.

Table3

Thermodynamic parameters characteristic to the sorption process of Pb(II) by natural hemp fibers

T, K	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
277	-20.035	14.21	0.123
298	-22.046		0.122
333	-25.292		0.122

The positive value of entropy change suggests the increase in randomness at the solid–liquid interface during the sorption of Pb(II) on natural hemp fibers.

CONCLUSIONS

The natural hemp may be considered as a reasonable sorbent for Pb(II) ions from diluted aqueous solutions. The pseudo–first order equation is better obeyed than the kinetic pseudo–second order.

The Pb(II) sorption process on the tested material follows Langmuir isotherm. The obtained values of isothermal thermodynamic parameters show that the Pb(II) retention is a spontaneous process of endothermic and chemical nature.

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