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INVESTIGATIONS ON THE POSSIBILITY OF NATURAL HEMP FIBERS USE FOR Zn(II) IONS REMOVAL FROM WASTEWATERS

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Abstract

Natural hemp fibers have been evaluated for Zn (II) ions sorption from diluted aqueous solutions. In order to establish the optimum conditions, the effect of initial pH of solution, hemp dose, Zn (II) concentration, temperature and contact time of phases on the Zn (II) sorption by natural hemp has been studied. To model the Zn (II) sorption at three different temperatures the Langmuir and Freundlich isotherms have been used. The Langmuir maximum sorption capacities were determined as being of 0.2545, 0.3238 and 0.3754 mmol/g at 5^0C, 20^0C and 50^0C, respectively. In order to evaluate the thermodynamic feasibility of the Zn (II) sorption process, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated on the basis of Langmuir constants. The constants of the pseudo first sorption rate, k', determined by means of Lagergren equation is $6.678x10^{-3}min^{-1}$. The results of this study suggest that the natural hemp can be efficiently used in the removal of Zn (II) ions from wastewaters with low content of the tested cation.

Key words: hemp fibers, isotherm, sorption, wastewaters

1. Introduction

With the current interest in environmental pollution, removal and/ or recovery of heavy metal ions from effluents is important in eliminating one of the major causes of water pollution. Among the other heavy metals, zinc is an essential mineral for all aerobic and anaerobic organisms. However, it has been proven that large amounts of zinc (II) can seriously affect the health of environment because of its toxicity (Gavrilescu, 2004).

Sorption has been evolved into one of the most effective methods for the removal and recovery of heavy metals from industrial and municipal effluents. The use of sorbents based on expensive synthetic polymers involves some major disadvantages among the fact that their manufacturing in itself is environmental – malign is of crucial importance.

Natural materials or waste products from industrial or agricultural activities can be used as alternative sorbents since they are inexpensive, abundant in nature, require little processing and can be disposed in a sustainable matter if is necessary (Bailey et al. 1999).

Among these materials peat, wood, tree bark, fibers of flax, cotton or jute, sand, sawdust, bauxite, bentonite clay, steel plant slag and fly ash can be numbered (Gene–Fuhrman et al., 2007; Hamadi et al., 2001; Khazali et al., 2007; Pehlivan et al., 2006; Sharma et al., 2007, Tofan et al., 2008) .

Hemp is another commonly available unconventional material that can be efficiently used in natural and modified forms for removal of Cr (III), Cu (II), Ag(I), Cd(II), Pb(II) ions from polluted waters (Paduraru, 2002; Tofan, 1999; Tofan, 2000; Tofan et al., 2001a; Tofan et al., 2001b; Tofan, 2004).

In this work the sorption and kinetic properties of natural hemp fibers in batch retention of zinc (II) ions from aqueous solutions have been assessed.

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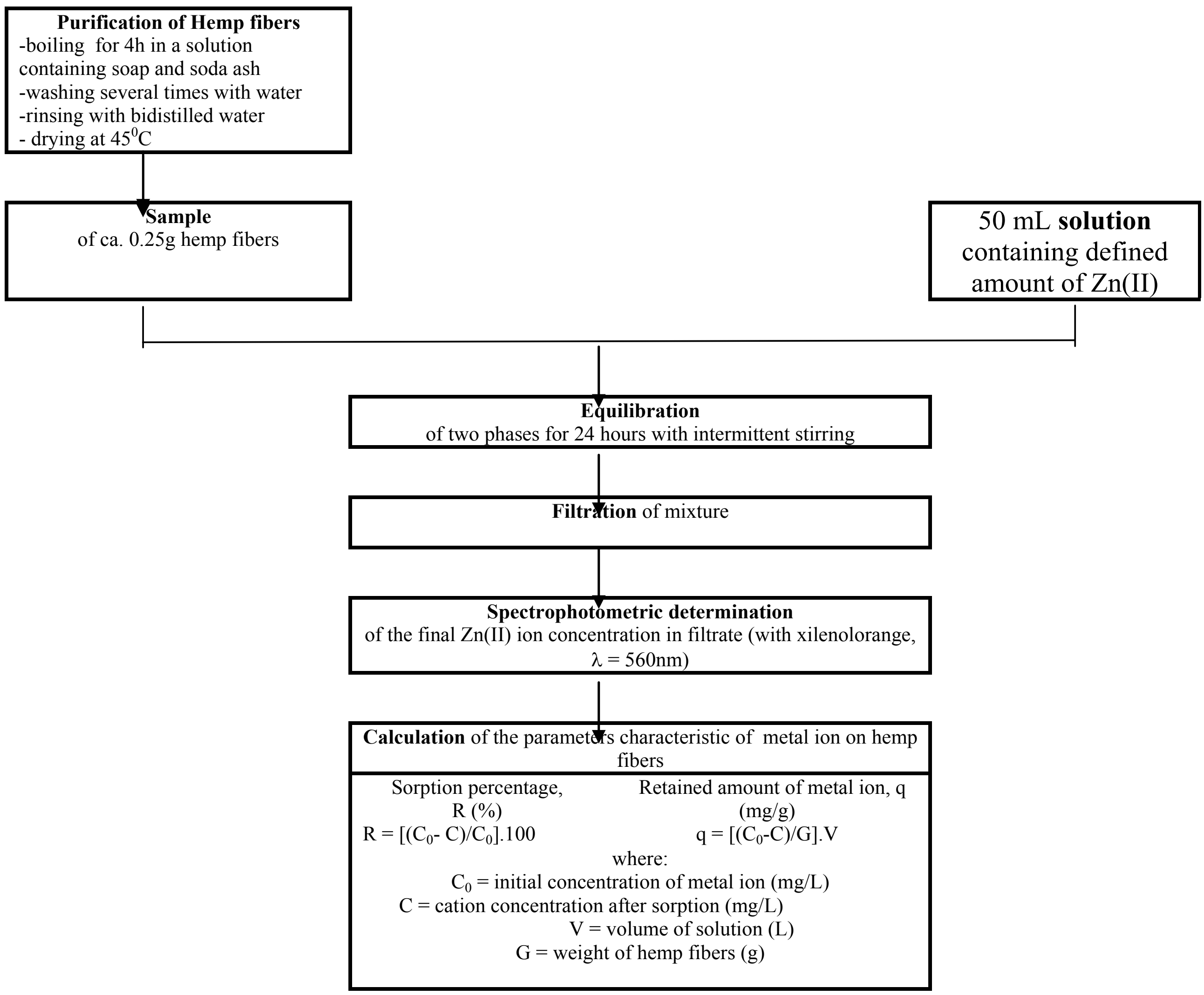

Fig.1. A schematic representation of the batch sorption procedure carried out in this study

The choice of hemp as a sorbent of study is based on its remarkable fundamental features: low cost, availability, high mechanical strength and porosity, hydrophilic character, fast sorption, tolerance to biological structures, easiness in functionalization, possibility of being used as fibers and filters.

2. Experimental

2.1. Materials and reagents

Hemp fibers were purified by boiling for 4h in a solution containing soap and soda ash, followed by washing several times with water, rinsing with doubly distilled water, drying in an oven at 45^0C.

Stock solution of 1mg Zn (II)/ mL was prepared by dissolution of 1.0652 g $ZnSO_4 \cdot 7H_2O$ and dilution to 250mL. Subsequently this solution was standardized gravimetrically. Working solutions were prepared by the requisite dilution of the stock solution.

2.2. Sorption Procedure

The sorption study of Zn (II) ions on natural hemp has been carried out in batch conditions, according to the procedure presented in Figure 1.

2.3. Apparatus

Absorbance measurements were performed on a S104D–WPA Linton Cambridge spectrophotometer. The solution pH has been measured with an M – 64 Radiometer pH – meter.

3. Results and discussion

The hemp fiber is a cellulosic natural plant fiber having the chemical composition recorded in Table 1. Fig. 2 shows the structure of the hemp fibers under study.

The idea of this unconventional natural cellulosic material use for the batch retention of zinc (II) ions is based on the presence of some potential chelating groups (hydroxyl, carbonyl, methoxy) in the structure of the cellulose and lignine structure.

Table 1. Chemical composition of hemp

Cellulose (%)	74-75	Ash (%)	0.82
Hemicellulose (%)	18.4-15.4	Xylans (%)	3.0- 7.0
Lignin (%)	3.7	Proteins (%)	0.5 – 1
Waxs (%)	4.04	Pectins (%)	4.0 – 8.0

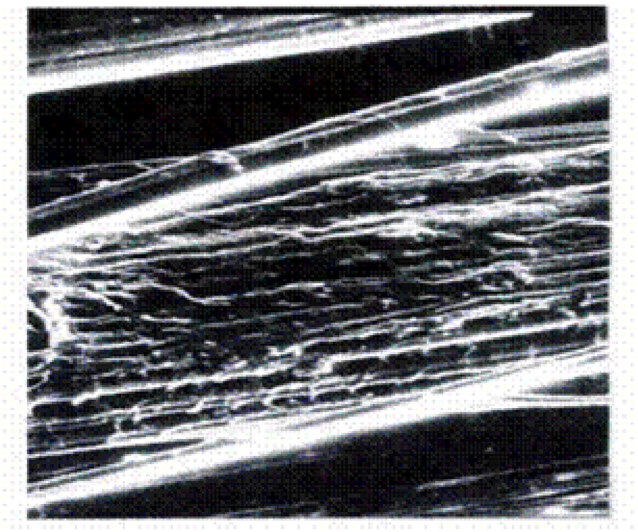

Fig. 2. Electronic micrograph of hemp fibers

In order to establish the optimum conditions of sorption, the effects of pH, adsorbent dose, metal concentration, temperature and contact time on the Zn (II) retention by natural hemp have been studied.

3.1. Effect of initial pH

The effect of solution acidity on Zn (II) sorption by untreated hemp was studied in the initial pH range of 2 – 5 and is shown in Fig. 3. In this pH range no $Zn(OH)_2$ precipitation takes place. According to the speciation data from literature, on solutions at pH 2-5, the studied metal exists in its double positively charged form (Zn^{2+}) (Ferguson, 1990).

As can be seen from Fig. 3, the smallest amount of retained Zn(II)(2.064mg/g) was found at pH=2 (reached by acidification with H_2SO_4 solution). Then the sorption increases with pH increasing. The highest Zn(II) retained amount (4.75mg/g) is reaching at initial pH=5 from unbuffered solutions. For this reason, the subsequent dependences have been studied from solutions of pH=5 obtained by the simple dilutions of initial solutions.

The pH dependence in the Zn(II)–natural hemp batch sorption system might be due to the dissociation of superficial functional groups, resulting in negative charges at the active sites on the hemp surface that would allow Zn^{2+} ion to be chemisorbed.

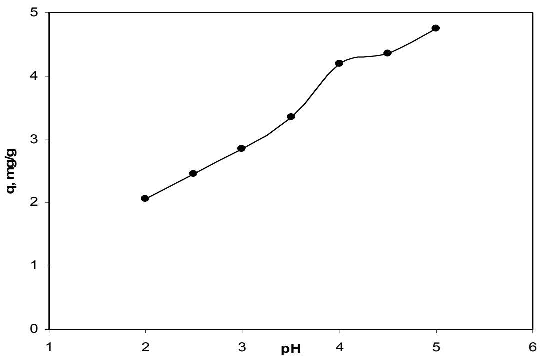

Fig. 3. Influence of initial pH on Zn (II) – natural hemp batch sorption system (C_0 = 40mg/L; 0.25 g of hemp; contact time = 24 hours)

3.2. Effect of hemp dose

The influence of hemp dose has been investigated from solutions of initial concentration equal to 80 mg/L. The resulting dependence is given in Fig. 4.

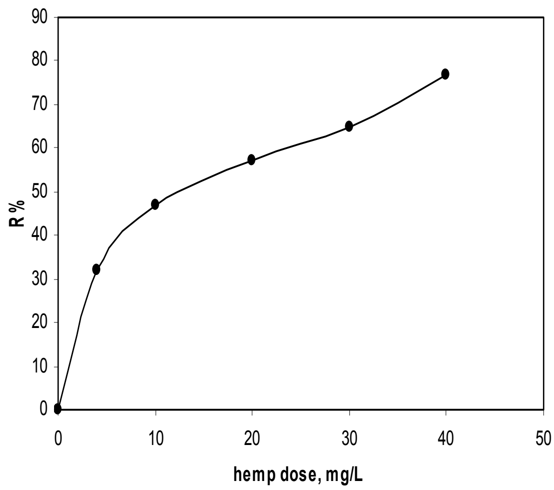

Fig. 4. Percentage of Zn(II) retention as function of hemp dose (pH = 5, C_0 = 80mg/L, time contact = 24h)

As follows from Fig.4, the values of the sorption percentage increased with increasing hemp dose. This trend is in good agreement with higher number of available sites of the natural hemp for zinc(II) binding. At the maximal dose of 40 mg hemp/L, the percentage of Zn (II) retention reached a value of 80 %.

3.3. Effect of initial Zn(II) concentration

The amount of Zn (II) retained on the hemp fibers (*q*) increased with increasing Zn(II) concentration in initial solution (Table 2).

On the other hand, the Zn (II) amount increasing results in the decrease of the sorption percentage, R% (Table 2).

The enhancement of the metal uptake on higher Zn (II) initial concentration might be due to the high values of initial number of Zn (II) mmoles /

limited number of available binding sites ratio. The access of Zn (II) ions is hindered probably by the occupation of the total active sites on the hemp. As a consequence, the percentages of Zn (II) retention decreased. This trend leads to the conclusion that the natural hemp can be efficiently used in the removal of Zn (II) ions from wastewaters with low contents of the tested cation.

Table 2. The effect of initial Zn(II) concentration on its sorption by natural hemp

C_0 (mg/L)	q, (mg/g)	R, %
20	2.85	75.2
40	5.25	70.1
60	7.25	64.2
80	8.56	60.0
100	9.25	55.1
120	10.3	49.2
160	11.75	41.5
180	12.0	34.8

3.4. Sorption modeling

To describe the equilibrium distribution of Zn (II) ions between the hemp phase and the aqueous solution phase, two different sorption models, Langmuir and Freundlich have been used.

Langmuir Isotherm

The most widely used isotherm equation for modelling of the sorption equilibrium data is the Langmuir two parameters equation (Langmuir 1916) (Eq. 1):

$$Q=\frac{q_0 \cdot K_L \cdot C}{1+K_L \cdot C} \qquad (1)$$

where q is the amount of cation sorbed per unit of sorbent at equilibrium (mmol/g); C is the equilibrium concentration of cation remaining in the solution (mmol/L) and q_0 and K_L are the Langmuir constants related to the sorption capacity and energy of sorption, respectively.

The Langmuir isotherms for Zn (II) cation sorption on the fibrous sorbent under study at three different temperatures are shown in Fig.5.

The validity of the Langmuir equation assumes that the uptake of Zn (II) ions on hemp occurs via formation of a monolayer coverage of the sorbate at the outer surface of the sorbent without any interaction between the sorbed ions.

The Langmuir equation can be liniarized as follows:

$$\frac{1}{q}=\frac{1}{q_0}+\frac{1}{K_L \cdot C} \qquad (2)$$

The linear form can be used for the linearization of experimental data by plotting 1/q against 1/C.

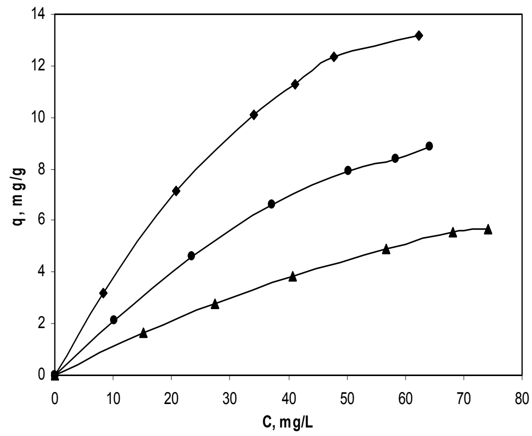

Fig.5. Langmuir isotherms for Zn(II) retention on natural hemp at different temperatures(t= 4^0C (▲); t= 50^0C (♦); t= 20^0C (·); hemp dose= 0.25g; pH=5)

The Langmuir constants can be evaluated from the slope and the intercept of linear equation. Table 3 characterized the Zn (II) sorption on hemp fibers at three different temperatures by means of Langmuir constants

Table 3. Description of Zn (II) sorption on hemp by means of Langmuir constants

T, K	q_0		K_L (L/mol)
	mmol Zn(II)/ g hemp	mg Zn(II)/ g hemp	
277	0.2545	16.54	474
293	0.3238	21.047	734.05
323	0.3754	24.401	1351.7

It is significant from Table 3 that the hemp is a reasonable sorbent for Zn (II) removal from aqueous solutions. The low values for the maximum capacity of sorption, q_0 (maximum amount of sorbed ion required to give a complete monolayer on a surface) are in good agreement with literature data reporting the retention of Cr(III), Cu(II), Ag(I) and Cd(II) ions on natural hemp (Paduraru, 2002; Tofan, 2000).

In this context, our attention has been focused on the improvement of hemp sorption capacity by physical and chemical treatment (Tofan, 1999; Tofan et al., 2001a; Tofan et al., 2001b; Tofan, 2004).

K_L is a measurement of relative sorption affinity being the Langmuir constant related to the energy of sorption. Its high values recorded in Table 3 involve strong bonds between sorbed Zn (II) ions and hemp.

Freundlich isotherm

The Freundlich isotherm is represented by Eq. (3) (Gupta et al., 2006):

$$lg\ q = lg\ K_F + (1/n)\ lgC \qquad (3)$$

where q is the amount of cation sorbed per unit gram of sorbent at equilibrium; C is the cation concentration left in solution at equilibrium; K_F (sorption capacity) and n (sorption intensity) are the Freundlich constants. If the sorption is favorable, then the ratios 1/n<1 or n >1, means that the forces within the surface layer are repulsive.

The plots of Equation (3) for the sorption of the tested cation on fibrous hemp at three different temperatures are given in Fig.6.

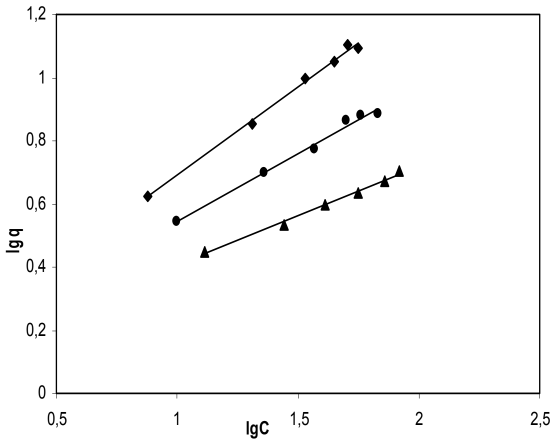

Fig. 6. Freundlich plots for sorption of Zn(II) ions by hemp fibers(t= 4^0C (▲); t= 50^0C (♦); t= 20^0C (·); hemp dose= 0.25g; pH=5)

The linear plots in Fig. 6 point out that the Zn (II) – natural hemp sorption system may be modeled by means of the Freundlich isotherm, too. Table 4 records the K_F and n values derived from the slope and the intercept of the linear Freundlich plots recorded in Fig.6.

Table 4. Freundlich constants characteristic to the Zn (II) retention on hemp fibers at different temperatures

T, K	*n*	K_F
323	1.78	1.34
293	2.33	1.30
277	3.13	1.23

As follows from Table 4, the values of n>1 indicated that the sorption capacity is only slightly suppressed at lower equilibrium concentrations. Saturated fibrous hemp with sorbed Zn(II) ions was no evident by this isotherm; thus infinite coverage is predicted mathematically, indicating multilayer sorption on the surface (Tsai et al., 2005).

3.5. Goodness of models fit

To compare the Langmuir and Freundlich isotherm models, the experimental data have been statistically processed by linear regression. The regression equations of y = ax +b type and the obtained values of the correlation coefficient, R^2, are given in Table 5. Obviously, it can be seen that the obtained data fit better to the Langmuir model than the Freundlich model (higher values for R^2).

3.6. Effect of temperature and thermodynamic parameters

The temperature has a favorable effect within the batch sorption systems under study (Figures 5 and 6). Both Langmuir and Freundlich constants increase with increasing temperatures, showing that the capacity of sorption and sorption intensity are enhanced at higher temperatures. In order to evaluate the thermodynamic feasibility of the Zn (II) sorption process on hemp, the thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated. On the basis of the values of Langmuir constants, K_L, at different temperatures, the following equations have been used (Hasany et al. 2002):

$$\Delta G = RTlnK_L \quad (4)$$

$$ln\ K_L = constant = -\Delta G/RT \quad (5)$$

$$\Delta S = (\Delta H-\Delta G)/T \quad (6)$$

where *R* is the gas constant and *T* is the absolute temperature.

The values obtained by equations (4-6) application are recorded in Table 6.

At all working temperatures, the *ΔG* values are negative, showing the spontaneous nature and the feasibility of Zn (II) sorption on hemp fibers. The positive values of ΔH indicate that the Zn (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 Zn (II) ions.

3.7. Effect of contact time of phases

Fig. 7 illustrates the influence of contact time on the Zn (II) retention from solutions with initial concentration of 80 µg/ mL and initial pH = 5 by natural hemp. It can be seen from Fig. 7 that the Zn(II) amounts retained on hemp increase with contact time of phases increasing. Usually, the kinetic data are treated with the aid of Lagergren equation (7):

$$lg(q_e - q_t) = lgq_e - k't/2.303 \quad (7)$$

where:
q_e and q_t are the amounts of Zn(II)(mg/g) sorbed at equilibrium and at any time(t), respectively and *k'* is the constant rate of sorption (min^{-1}).

The kinetic parameters derived from the linear Lagergren plot of lg(q_e – q_t) against t are listed in Table 7. The data from Table 7 point out that the Zn(II) sorption process on hemp is of pseudo – first order with respect to the concentration.

Table 5. Statistical analysis

T, K	*Langmuir isotherm*		*Freundlich isotherm*	
	Linear regression equation	R^2	Linear regression equation	R^2
323	y= 3.9281x+8.2659	0.9988	y = 0.5611x + 0.1283	0.9945
293	y = 3.0876x+4.2063	0.9973	y = 0.429x + 0.1147	0.9891
277	y = 2.6634x+1.9705	0.9976	y = 0.3125x + 0.0933	0.9925

Table 6. Thermodynamic characterization of the sorption process of Zn (II) on natural hemp

T, K	*ΔG (kJ/mol)*	*ΔH (kJ/mol)*	*ΔS (J/mol.K)*
278	- 14.183		112
293	- 16.066	16.98	112
323	- 19.350		112

The results obtained in this study are significant for future development of the natural hemp into beneficial material for environmental applications.

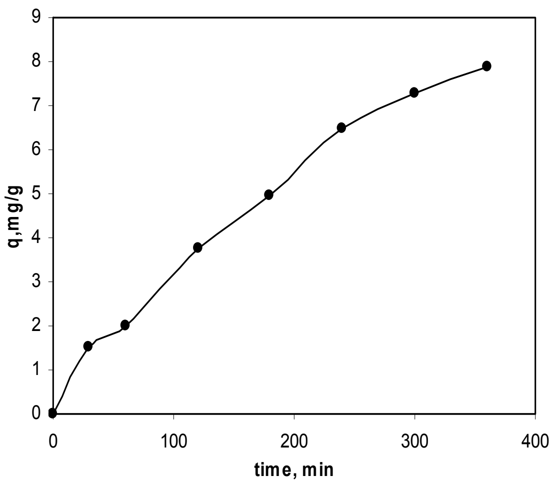

Fig. 7. The effect of contact time of phases on the Zn(II) – natural hemp batch sorption system (hemp dose=0.25g; pH=5)

Table 7. Kinetic description of the Zn(II) sorption process by means of Lagergren equation

t, min	*lg (q_e- q_t)*	*Linear regression equation*	*R^2*
30	0.82	y = -0.0029x +0.9423	
60	0.75	q_e = 8,56	0.9963
120	0.59	***k'*** = 6,678x10^{-3} min^{-1}	
180	0.44		
240	0.26		
300	0.085		
360	-0.052		

4. Conclusions

Natural hemp exhibits reasonable sorption properties with potential applicability in removal/ recovery of Zn (II) ions from wastewaters. In the studied initial pH range of 2-5 the sorption increases with pH increasing. The highest Zn (II) retained amount (4.75mg/g) is reaching at initial pH=5 from unbuffered solutions. The values of the sorption percentage increase with increasing hemp dose.

The amount of Zn(II) retained on the hemp fibers increase with increasing Zn(II) concentration in initial solution, but the sorption percentages decrease.

The Langmuir and Freundlich isotherms were used to model the sorption equilibrium. The results indicated that the Langmuir model has a better correlation with the experimental data than the Freundlich model. The values obtained for the thermodynamic parameters point out the spontaneous and endothermic nature of the Zn (II) sorption process, favoured by temperature increasing.

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