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Biosorption of heavy metal ions from aqueous solutions by short hemp fibers: Effect of chemical composition

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ABSTRACT

Sorption potential of waste short hemp fibers for Pb^{2+}, Cd^{2+} and Zn^{2+} ions from aqueous media was explored. In order to assess the influence of hemp fiber chemical composition on their heavy metals sorption potential, lignin and hemicelluloses were removed selectively by chemical modification. The degree of fiber swelling and water retention value were determined in order to evaluate the change in accessibility of the cell wall components to aqueous solutions due to the fiber modification. The effects of initial ion concentration, contact time and cosorption were studied in batch sorption experiments. The obtained results show that when the content of either lignin or hemicelluloses is progressively reduced by chemical treatment, the sorption properties of hemp fibers are improved. Short hemp fibers are capable of sorbing metal ions (Pb^{2+}, Cd^{2+} and Zn^{2+}) from single as well as from ternary metal ion solutions. The maximum total uptake capacities for Pb^{2+}, Cd^{2+} and Zn^{2+} ions from single solutions are the same, i.e. 0.078 mmol/g, and from ternary mixture 0.074, 0.035 and 0.035 mmol/g, respectively.

1. Introduction

The discharge of toxic heavy metals into the environment is a serious pollution problem affecting water and soil quality, hence presenting a direct danger to human health. Ions of cadmium (Cd^{2+}), lead (Pb^{2+}) and zinc (Zn^{2+}), which are most frequently present in the wastewaters, can cause renal dysfunction as well as chronical alterations in nervous system and gastrointestinal tract, even at low concentrations. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. These techniques, apart from being economically expensive, have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed in order to reduce heavy metal content. A search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial byproducts, as potential metal sorbents [1–6].

The usage of biosorbents is an alternative to conventional methods. The term "biosorbent" includes the usage of dead biomass (such as fibers, peat and rice hulls) as well as living plants and bacteria as sorbents. Biosorbents represent cheap filter materials often with high affinity and capacity, and they are already available in most places. Some types of biosorbents are broad range with no specific priority of metal ion bonding, while others can be specific for certain types of metal ions. There are some limitations pertaining to the usage of living organisms as sorbents, e.g. they cannot function at low pH level, or at toxic levels of metal ions, while plant fibers on the contrary are chemically and physically more robust [1,2,7]. Plant fibers consist mainly of cellulose, hemicelluloses, lignin, and some pectin and extractives (fat, waxes, etc.). Metal ions sorb mainly to carboxylic (primarily present in hemicelluloses, pectin and lignin), phenolic (lignin and extractives) and to some extent hydroxylic (cellulose, hemicelluloses, lignin, extractives and pectin) and carbonyl groups (lignin). Strong bonding of metal ions by the hydroxylic, carboxylic and phenolic groups often involves complexation and ion exchange [8–11].

In many laboratory tests of metal ion sorption by lignocellulosic fibers, unmodified and modified coir, jute, kenaf and ramie have been used [8,9,12]. However, few literatures were found so far about the sorption of heavy metals by hemp fibers [13] and much more about bio-accumulation and phytoremediation of heavy metal polluted soil by cultivation of hemp or flax [14–17].

Hemp fibers are traditionally used for production of textiles. From the economic aspect hemp presents a high-productive cul-

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ture. Nowadays, there is an increasing interest in total exploitation of the plant, with the intention of using seeds, fiber and shive as raw materials. The increased production of hemp fibers brought about an increase in the amount of waste, namely shives, short and entangled fibers. Short and entangled fibers are very convenient for filter production, either from ecological and economical aspects, or because of their properties. Our preliminary investigations have shown that short hemp fibers have a high potential of heavy metal ions uptake from aqueous solutions [18].

The objectives of the present investigation were to quantify the sorption potential of modified and unmodified short hemp fibers for heavy metal ions (Pb^{2+}, Cd^{2+} and Zn^{2+}) with particular focus on sorption kinetics and cosorption. In order to assess the influence of hemp fiber chemical composition on their heavy metal ions sorption potential, hemp fibers with different contents of either hemicelluloses or lignin were obtained by chemical treatment with 17.5% sodium hydroxide or 0.7% sodium chlorite. Accessibility of the cell wall components to aqueous solutions, which is very important for the removal of heavy metal ions from their aqueous solutions, was evaluated by determination of the degree of fiber swelling and water retention value.

2. Materials and methods

2.1. Material

The fibers used in this investigation were short and entangled hemp fibers obtained from ITES Odzaci, Serbia. Chemical composition of used fibers are: water solubles, 1.50%; fats and waxes, 0.69%; pectins, 1.39%; α-cellulose, 78.15%; lignin, 6.06%; hemicelluloses, 10.72%. All used chemicals are p.a. grade.

2.2. Chemical treatment

Hemp fibers were modified by chemical treatments in order to gradually remove either hemicelluloses or lignin. The progressive removal of the hemicelluloses and keeping the lignin content unchanged was brought by treating the fiber samples with 17.5% NaOH solution, 1:50 liquor ratio, at room temperature, for 5 and 45 min, followed by neutralisation with 1% acetic acid, washing and drying [19]. The progressive removal of lignin and keeping the hemicelluloses content unchanged was achieved by treating hemp fibers with 0.7% $NaClO_2$ at pH 4, 1:50 liquor ratio, at boil temperature, for different periods of time (5 and 60 min), followed by washing and drying [19]. The chemical treatment scheme and list of samples are shown in Table 1.

2.3. Determination of weight loss and chemical composition

Loss in weight, as result of chemical treatment, was determined by the direct gravimetric method [20]. Chemical composition of unmodified sample and each of the modified samples was determined according to the scheme of Soutar and Bryden [19] by successive removal of water solubles, fats and waxes, pectins, lignin and hemicelluloses. The results were the average of three parallel determinations.

Table 1
The chemical treatment scheme and list of samples

Modification conditions			Sample code
Concentrations and modification means	Temperature	Time (min)	
Unmodified (control) sample	–	–	C
17.5% NaOH	Room temperature	5	H17.5R5
		45	H17.5R45
0.7% $NaClO_2$	Boiling temperature	5	L0.7B5
		60	L0.7B60

2.4. Determination of swelling kinetics and water retention value of hemp fibers

Swelling kinetics was determined by measuring fiber diameters before (d_0, μm) and after (d_t, μm) swelling in distilled water during defined periods of time: 5, 10, 15, 20, 30 and 60 min. For measurement of hemp fiber diameters the light microscope "Ergaval" (Carl Zeiss-Jena, Ltd., Austria), equipped with an ocular micrometer, was used. Degree of fiber swelling (DS) was calculated using following Eq. (1):

$$\mathrm{DS} = \frac{d_0 - d_t}{d_0} \cdot 100\,[\%] \quad (1)$$

Water retention of hemp fibers was determined by standard centrifuge method [21].

2.5. Metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}) sorption experiments

Sorption of heavy metal ions (Pb^{2+}, Cd^{2+} and Zn^{2+}) was performed from aqueous solutions of $Cd(NO_3)_2 \times 4H_2O$; $Pb(NO_3)_2$ and $Zn(CH_3COO)_2 \times 2H_2O$, at room temperature, for different periods of time (3, 5, 10, 15, 30, 60 and 120 min). The initial concentrations of each of the solutions cited were: 0.05, 0.10 and 0.20 mmol/L. All the experiments were carried out in batch process. Hemp fiber sample (0.5 g) was shaken in 200 mL of aqueous solution containing a single metal ion of defined concentration. Taking into account the fact that in real conditions wastewaters contain mainly mixtures of heavy metals, in the second group of experiments, competitive sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from solutions containing the same amount of each metal ion was investigated. Also, the effect of pH on the biosorption was studied. For this, the initial pH of 5.5 of each metal ion aqueous solution was adjusted by stepwise addition of HNO_3 or NH_4OH.

The metal ion uptake (q, mmol/g) was determined as the difference between the initial concentration of metal ions in solution (c_0, mmol/L) and the final concentration of metal ions in the solution after defined time (c_t, mmol/L) (Eq. (2)). Atomic Absorption Spectrometer—Pye Unicam SPC (Pye Unicam, Ltd., UK) was used for the determination of metal ions concentration in the solution.

$$q = (c_0 - c_t) \cdot \frac{V}{m}\,[\mathrm{mmol/g}] \quad (2)$$

In Eq. (2) V is the solution volume (L) and m is the weight of sorbent material (g). Sorption efficiency (SE, %) was determined as the quotient of the final concentration of metal ions in the solution after defined time (c_t, mmol/L) and the initial concentration of metal ions in solution (c_0, mmol/L) (Eq. (3)).

$$\mathrm{SE} = \frac{c_t}{c_0} \cdot 100\,[\%] \quad (3)$$

3. Results and discussion

3.1. Influence of chemical treatment on chemical composition of hemp fibers

The chemical compositions of modified hemp fibers and those of the control sample, and the weight loss are given in Table 2.

From results shown in Table 2, it is obvious that during hemp fibers treatment with 17.5% NaOH hemicelluloses were progres-

Table 2
Chemical composition and weight loss of hemp and modified hemp fibres

Sample code	α-Cellulose content (%)	Hemicelluloses		Lignin		Weight loss (%)
		Content (%)	Removed (%)	Content (%)	Removed (%)	
C	78.15	10.72	–	6.06	–	–
H17.5R5	80.59	4.69	56.25	5.66	6.60	8.15
H17.5R45	79.70	3.59	66.51	5.41	10.73	9.90
L0.7B5	80.03	8.89	17.07	4.09	32.51	4.16
L0.7B60	79.15	8.99	16.14	3.09	49.01	6.17

sively removed, their content decreased for approximately 70% in relation to unmodified fibers. Lignin content decreased slightly, because of its low reactivity. Namely, degradation of lignin during the alkaline treatment is impeded by the presence of strong carbon–carbon linkages and other chemical groups such as aromatic groups, which are very resistant to chemical attack [22].

On the other hand, treatment of hemp fibers with 0.7% $NaClO_2$ progressively removed lignin for about 50% in relation to unmodified fibers. It has to be mentioned that in this case the content of hemicelluloses in modified hemp fibers decreased for about 17%.

During both types of hemp fibers modification, noncellulosic component content in modified fibers decreased in relation to unmodified hemp fibers, proportionally to the increase of modification time. Removing different amounts of hemicelluloses and lignin by chemical modification changed both chemical and physical properties of hemp fibers.

The severity of the treatment is generally characterized by weight loss. Loss in weight, as result of chemical treatment (Table 2), in both cases increased with the increase of time of treatment. Also, the alkaline treatment of hemp fibers results in higher weight loss in comparison to the sodium chlorite treatment.

3.2. Degree of swelling and water retention capacity of short hemp fibers

Lignocellulosic fibers are, generally, hygroscopic and have an affinity to water. Water is able to permeate into the non-crystalline portion of cellulose and all of the hemicelluloses and lignin. Thus, through adsorption and absorption, aqueous solution comes into contact with a very large surface area of different cell wall components [12]. Accessibility of the cell wall components to aqueous solutions is very important for the removal of heavy metal ions from their aqueous solutions, and can be assessed by determining the degree of fiber swelling and water retention value.

The degree of fiber swelling yields information on the extent of areas accessible to aqueous solutions within hemp fiber. Changes in the degree of fiber swelling of modified hemp fibers reflect changes in chemical composition, crystallinity, and pore structure. In Fig. 1 the kinetics of swelling of unmodified and the modified hemp fibers is presented.

From the data presented in Fig. 1 it is evident that the degree of swelling of all modified samples is higher in relation to the unmodified hemp fibers. Also, maximum swelling of unmodified hemp fibers is attained after 10 min from immersing in water, while all modified hemp fibers attained maximum swelling already after 5 min.

The increase of the degree of swelling of hemp fibers modified with 17.5% NaOH is the most likely consequence of removing the hemicelluloses from interfibrillar regions, followed by swelling and shrinkage of ultimate cells, which result in some disorientation of the fibrils and changes of amorphous and crystalline regions ratio, in favor of amorphous ones [23,24]. Also, during alkaline treatment of hemp fibers, lignin content decreased for 7–11% (Table 2), which together with the removal of fats and waxes, influences to a certain degree the increase of modified hemp fibers swelling. The degree of swelling of hemp fibers samples H17.5R5 and H17.5R45 is higher for 77% and 130%, respectively, in relation to the unmodified fibers. The increase of degree of hemp fiber swelling with the increase of time of treatment is very pronounced, and can be explained by removing the hemicelluloses and hydrophobic components during the alkaline treatment. Once when hemicellulosic components have been progressively removed, interfibrillar regions become less dense and less rigid, which with the greater content of amorphous regions enable easier penetration of larger quantity of water molecules into hemp fiber structure.

The degree of swelling of hemp fiber samples treated with 0.7% $NaClO_2$ samples L0.7B5 and L0.7B60 is higher for about 68% and 78%, respectively, in relation to the unmodified fibers. In hemp fibers modified with 0.7% $NaClO_2$ progressive removal of lignin occurred mostly in the middle lamella. The decrease of lignin content for almost 50% and of hemicelluloses for approximately 17% influenced changes in hemp fiber structure; these changes influence an increase of degree of swelling in relation to the unmodified fibers. In this case the duration of hemp fiber treatment did not influence the change of degree of swelling to a large extent. It can be noted that the degree of swelling of hemp fibers modified with 0.7% $NaClO_2$, for both intervals of time, is lower in relation to the 17.5% NaOH treated fibers degree of swelling. That could be ascribed to the fact that in this case a greater part of hemicelluloses remained in the interfibrillar regions and their densities have not been reduced as in fibers treated with 17.5% NaOH, which caused more difficult penetration of water molecules in these regions [24].

When hemp fibers are immersed in water they swell and imbibe considerably more water than they are capable to hold. The total water holding capacity of a fiber can be estimated by determining water retention values. All water absorbing and holding surfaces, cracks, and cavities are included with the water retention measure-

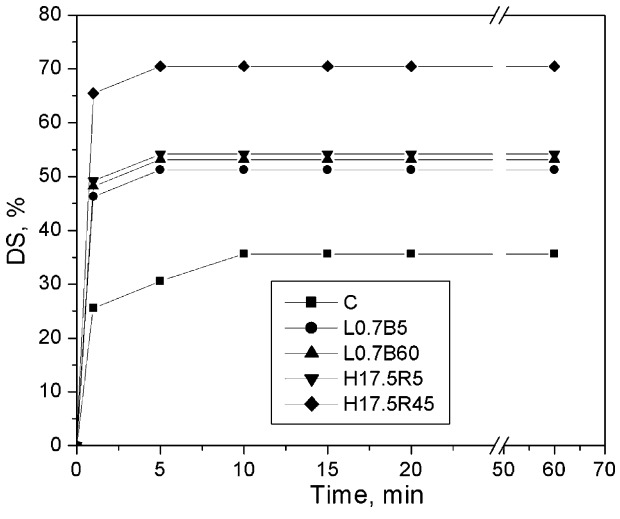

Fig. 1. Degree of swelling of unmodified and modified hemp fibers.

ment. Water retention values for all samples tested are shown in Fig. 2.

The alkali treatment (hemicelluloses removal) yielded water retention values the same or lower than the value of unmodified hemp fibers. Hemp fiber sample H17.5R5 has an almost unchanged water retention capacity in relation to unmodified fiber (sample C). With an increase of modification time, water retention value decreases so that the sample H17.5R45 has approximately for 15% lower water retention value in relation to the unmodified sample. The decrease of water retention value of hemp fibers modified with 17.5% NaOH with an increase of modification time is a consequence of structure changes, i.e. changes in the size and number of pores and microcracks in fibers during their modification. It is also worth to mention that this treatment reduces the content of hydrophilic components, hemicelluloses and pectins.

The effect of lignin removal on water retention value was significant, since removing about 50% of lignin results in 20% more water kept by modified hemp fibers in comparison with unmodified fibers. The higher water retention values of hemp fibers with lower lignin content presented in Fig. 2 can be explained by lignin removal from the middle lamella followed by fibrillation. Occurred fibrillation increased the roughness of hemp fiber surfaces and induced new capillary spaces in inter-surfacial layer between completely or partially separated fibers within the modified technical hemp fiber [22,24].

3.3. Biosorption performance of short hemp fibers

Biosorption is not restricted to one sorption mechanism only, but comprises several mechanisms such as ion exchange, chelation, precipitation, sorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of structural lignin and polysaccharide networks. Therefore, biosorption of heavy metal ions by lignocellulosics is affected by several factors such as initial pH, initial metal ion concentration, contact time, temperature, fiber pretreatment, etc. [7,8].

The effect of the solution pH on the metal ions sorption (Cd^{2+}, Pb^{2+} and Zn^{2+} ions) by short hemp fibers is illustrated in Fig. 3, for metal ions concentration of 0.1 mmol/L. As seen in the figure, metal ions sorption was strongly dependent on the solution pH. Cd^{2+}, Pb^{2+} and Zn^{2+} ions uptake by hemp fibers showed a sharp increase from negligible or very low to maximum values in the pH range of 2–5.5. This can be explained by the fact that the pH of the biosorption medium affects the solubility of metal ions and the ionization state of the functional groups of the hemp fibers [25]. Because of high proton concentration at lower pH, heavy metal biosorption decreases due to the positive charge density on metal binding sites (i.e. hydrogen ions compete effectively with metal ions in binding to the sites) and at a low pH, of almost 2.0, all binding sites may be protonated, thereby desorbing all originally bounded metals from the fibers. The negative charge density on the fiber surface increases with increasing pH due to deprotonation of the metal binding sites. The metal ions then compete more effectively for available binding sites, which increases biosorption. The high sorption levels for the short hemp fibers between pH 4.0 and 5.5 indicate that a high affinity for metal ions predominates in this pH region. When the initial pH of the solution was adjusted to a value higher than pH 6.5, ions precipitated because of the higher concentration of OH^- ions in the sorption medium and hence studies in this range was not conducted. Because of the fact that the short hemp fibers have a maximum sorption for metal ions at pH 5.5 this pH value was selected for further experiments.

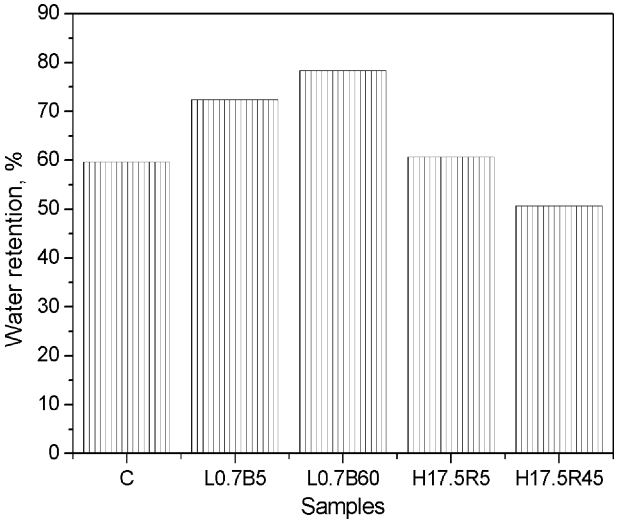

Fig. 2. Water retention values of unmodified and modified hemp fiber samples.

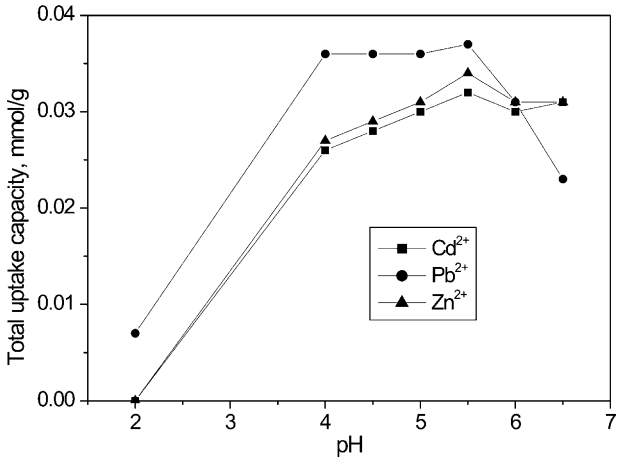

Fig. 3. Effect of initial pH on the Cd^{2+}, Pb^{2+} and Zn^{2+} ions sorption on unmodified hemp fibers (initial concentration of solution 0.1 mmol/L, RT, contact time 2 h).

The effect of the contact time and the initial metal ion concentration was studied up to a contact time of 2 h and using solutions containing 0.05, 0.1 and 0.2 mmol/L of each metal ion (Fig. 4). Rapid biosorption of Cd^{2+}, Pb^{2+} and Zn^{2+} ions was observed in the first 5 min; approximately more than 80% of the total uptake capacity of metal ions was sorbed within this period of time. This rapid initial biosorption is consistent with the previous reports on the biosorption of Cd^{2+}, Pb^{2+} and Zn^{2+} ions [8,25]. Depending on initial metal ion concentration, system attained equilibrium in 10 min for concentration of 0.05 mmol/L and 30 min for concentration of 0.1 and 0.2 mmol/L. The generally fast sorptions indicate that reactions at outer surfaces are important. After this equilibrium period the amount of sorbed metal ions did not change significantly with an increase in contact time.

The experimental results of biosorption of Cd^{2+}, Pb^{2+} and Zn^{2+} ions by short hemp fibers at various initial metal ion concentrations show that with an increase of the initial solution concentrations, the total uptake capacity of metal ions also increased (Fig. 5). For instance, changing the initial concentration from 0.05 to 0.2 mmol/L, caused an increase of the amount of Cd^{2+}, Pb^{2+} and Zn^{2+} ions sorbed by H17.5R5 from 0.019 to 0.056, 0.020 to 0.078 and 0.019 to 0.060 mmol/g, respectively. Also, the total uptake capacity of Cd^{2+} and Zn^{2+} ions is increased by hemp fibers modification (i.e. the separate removal of hemicelluloses and lignin), while at the same time the total uptake capacity of Pb^{2+} ions is almost unchanged. From Fig. 5c it can be seen that sample H17.5R60 sorbed the same

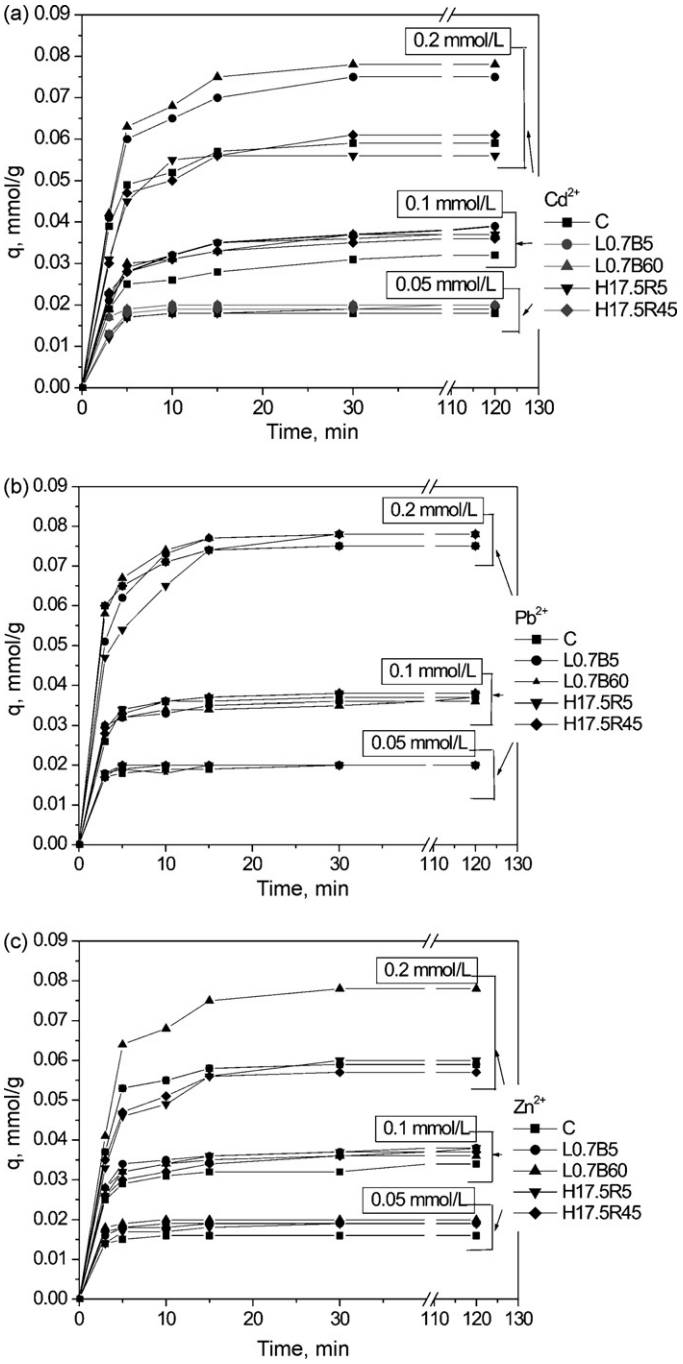

Fig. 4. Kinetics of Cd^{2+} (a), Pb^{2+} (b) and Zn^{2+} (c) sorption by unmodified and modified hemp fibers at initial concentration of 0.05, 0.1 and 0.2 mmol/L (pH 5.5, RT).

amount of Cd^{2+}, Pb^{2+} and Zn^{2+} ions (0.078 mmol/g). Data obtained from modification experiments in this study indicated that modification with sodium chlorite (i.e. removal of lignin) resulted in better improvement in biosorption capacities compared to alkali modification. This can be explained by the domination of sorption at outer surfaces of fibers, as we mentioned earlier, and increased the roughness of hemp fiber surfaces and induced new capillary spaces in inter-surfacial layer between completely or partially separated fibers due to the removal of lignin from the middle lamella, followed by fibrillation. Also, sodium chlorite oxidation of residual lignin that caused benzene ring cleavage and formation of dicarboxylic groups [26] should not be neglected. Taking in consideration all above mentioned and complexity of the structure and composition of hemp fibers, a simple relation between the lignin and hemicelluloses contents and the sorption capacity could not be demonstrated.

The results of the total uptake capacity of Cd^{2+}, Pb^{2+} and Zn^{2+} ions for non-competitive conditions indicate that all samples exhibit capacities which are influenced by the investigated metal ion, but these differences are significant only at the highest ions

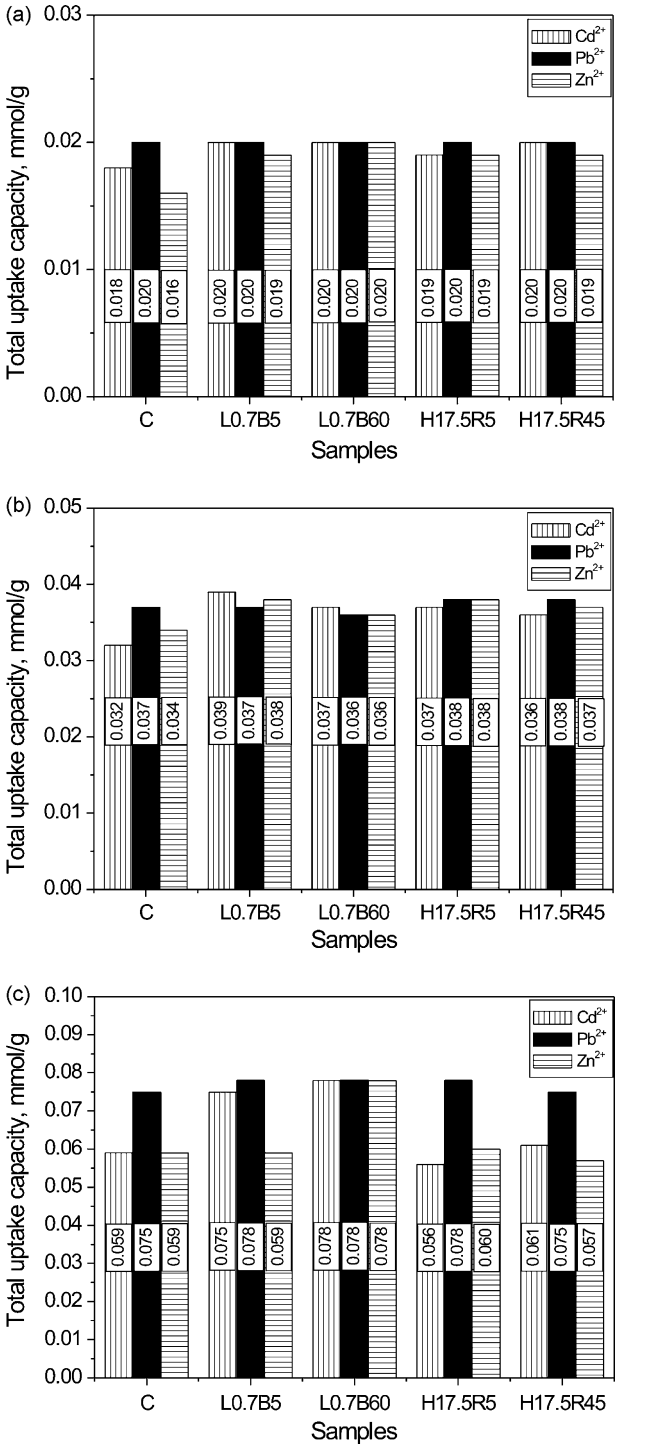

Fig. 5. Total uptake capacity of Cd^{2+}, Pb^{2+} and Zn^{2+} ions by unmodified and modified hemp fibers at initial concentration of 0.05 mmol/L (a), 0.1 mmol/L (b), and 0.2 mmol/L (c) (pH 5.5, RT, contact time 2 h).

concentration (0.2 mmol/L). This is because the ratio of the initial quantity of metal ions moles to the available binding sites is low at lower concentration and subsequently the sorption is less dependent on metal ion affinity. The exception is the sodium chlorite modified sample (L0.7B60) with the same affinity for Cd^{2+}, Pb^{2+} and Zn^{2+} ions.

The selectivity of unmodified and modified hemp fibers for metal ions (Cd^{2+}, Pb^{2+} and Zn^{2+}) is more pronounced and can be easily seen in the case of simultaneous biosorption of the ternary mixture, in which three metal ions compete for a limited number of binding sites (Fig. 6). The biosorption capacities of hemp fibers in the presence of the ternary mixture were lower for Cd^{2+} and Zn^{2+} ions than those for noncompetitive conditions, and almost the same for Pb^{2+} ions (compare Fig. 5 with Fig. 6). Also, an increase in metal ions concentration from 0.1 to 0.2 mmol/L in the competitive conditions caused about a twofold increase in the total uptake capacity of Pb^{2+} ions, while the total uptake capacities of Cd^{2+} and Zn^{2+} ions stayed almost unchanged (Fig. 6). The order of the affinity for competitive conditions was as follows: $Pb^{2+} > Cd^{2+} > Zn^{2+}$, which is in agreement with literature data [27,28].

The sodium chlorite modified sample (L0.7B5) demonstrated the best sorption properties; its total uptake capacities were 0.074 mmol/g for Pb^{2+}, 0.035 mmol/g for Cd^{2+}, and 0.035 mmol/g for Zn^{2+} ions from solution contained 0.2 mmol/g of each metal ion. However, for the evaluation of short hemp fibers suitability as sorbent material, besides uptake capacities, sorption efficiency should

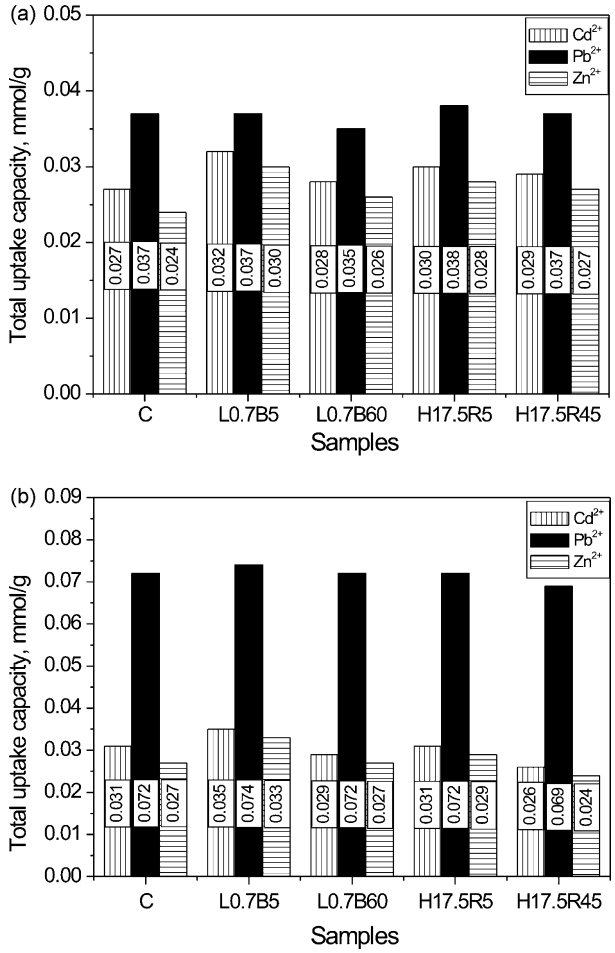

Fig. 6. Total uptake capacity of Cd^{2+}, Pb^{2+} and Zn^{2+} ions by unmodified and modified hemp fibers at ternary ion mixture of initial concentration 0.1 mmol/L (a) and 0.2 mmol/L (b) of each metal ion (pH 5.5, RT, contact time 2 h).

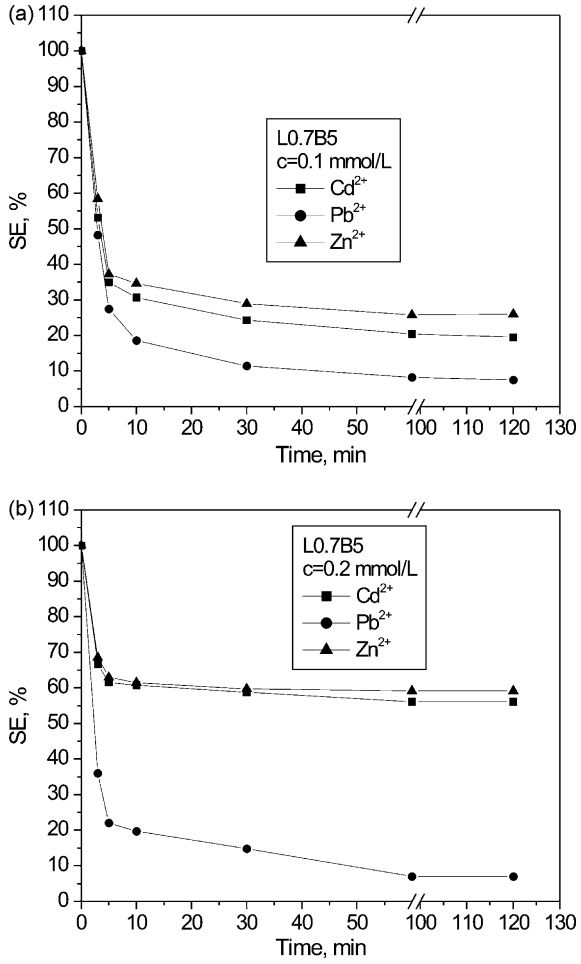

Fig. 7. Dependence of Cd^{2+}, Pb^{2+} and Zn^{2+} ions sorption efficiency on time of sorption, for the sample L0.7B5 from the ternary mixture of initial concentration: 0.1 mmol/L (a) and 0.2 mmol/L (b) of each metal ion.

be known. The dependence of the sorption efficiency of Cd^{2+}, Pb^{2+} and Zn^{2+} ions on time for this sample (L0.7B5), from solution contained 0.1 and 0.2 mmol/g of each metal ion, is shown in Fig. 7. The highest sorption efficiency of all the three ions from mixture, at initial 0.1 mmol/L concentration of mixture was attained after 60 min. In that moment in solution remained 19.51% of Cd^{2+} ion, 7.50% of Pb^{2+} ion and 26.00% of Zn^{2+} ion. At initial concentration of the ternary mixture contained 0.2 mmol/L of each metal ion, the highest sorption efficiency of Cd^{2+} and Pb^{2+} ions was attained after 60 min also while the sorption of Pb^{2+} ion was slightly faster (30 min). After attaining maximum sorption efficiency, in this case, in solution remained 56.10% of Cd^{2+} ion, 6.99% of Pb^{2+} ion and 59.16% of Zn^{2+} ion.

It is difficult to compare data from different literature sources since sorption of heavy metals is highly dependent on temperature, heavy metal concentration and contact time and researchers do not use identical conditions. However, it is interesting to note that sorption capacity of short hemp fibers for heavy metal ions was higher than that of activated carbon in the granular or powder form [25], or comparable with that of carbon nanotubes [29].

4. Conclusion

The use of short hemp fibers as biosorbent may offer an effective way to decrease Pb^{2+}, Cd^{2+} and Zn^{2+} ion concentration in wastewaters. Differently modified hemp fibers were evaluated in

terms of water and metal ions uptake capacities. The obtained results show that hemicellulose removal increases the degree of fiber swelling and decreases the water retention value of hemp fibers, while lignin removal decreases the degree of fiber swelling and increases the water retention ability of hemp fibers. A simple relation between lignin and hemicellulose contents and the uptake capacities for heavy metal ions could not be demonstrated.

Short hemp fibers are capable of sorbing metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}) from single as well as ternary metal ion solutions. The maximum total uptake capacities for Pb^{2+}, Cd^{2+} and Zn^{2+} ions from single ion solutions are the same and valued at 0.078 mmol/g. The biosorption capacities of hemp fibers in the presence of the ternary mixture are lower for Cd^{2+} and Zn^{2+} ions than that of noncompetitive conditions, and almost the same for Pb^{2+} ions. The sodium chlorite modified sample demonstrated the best sorption properties, its total uptake capacities were 0.074 mmol/g for Pb^{2+}, 0.035 mmol/g for Cd^{2+} and 0.035 mmol/g for Zn^{2+} ions from solution contained 0.2 mmol/L of each metal ion. The uptake of metal ions was very fast. Within the first 5 min of contact, approximately more than 80% of the total uptake of metal ions was sorbed.

Besides this paper proved good sorption properties, short hemp fibers, as the waste material from textile industry, have very low price in comparison with commercial sorbents and this advantage highly recommended their use for purification of wastewater.

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Appendix A. Nomenclature

Weight loss: In this paper, the weight loss was determined on atmospherically conditioned hemp fibers after different modification processes and calculated from the differences in weight using the following equation:

$$w_i = \frac{w_{\text{pre}} - w_{\text{after}}}{w_{\text{pre}}} \cdot 100\,[\%]$$

where w_i is the weight loss percentage, w_{pre} the weight of the conditioned fibers prior to modification and w_{after} is the weight after modification.

Degree of fiber swelling: When fibers absorb water, they change in dimensions, swelling transferely and/or axially. The swelling may be expressed in terms of the increase in diameter, area, length, or volume. In this paper we used transverse diameter swelling (DS) which was calculated by means of the following equation:

$$\text{DS} = \frac{d_0 - d_t}{d_0} \cdot 100\,[\%]$$

where d_0 (μm) is the diameter before and d_t (μm) is the diameter after swelling in distilled water during defined periods of time.

Water retention value: When fibers are immersed in water they swell and imbibe considerably more water, than they are capable of holding. The total water holding capacity of a fiber can be estimated by determining water retention values. The water retention value (WRV) represents the quantity of water which is retained in the fibers after the prescribed soaking in the water, and centrifugation. In this paper WRV was determined according to ASTDM D 2402-78 standard. The results were calculated using the following equation:

$$\text{WRV} = \frac{m_c - m_a}{m_a} \cdot 100\,[\%]$$

where m_c is the weight of centrifuged sample (g) and m_a is the weight of the absolute dry fibers (g).

Metal ion uptake: The metal ion uptake (q, mmol/g) is amount of metal ions sorbed by fibers from aqueous solutions and it was determined as the difference between the initial concentration of metal ions in solution (c_0, mmol/L) and the final concentration of metal ions in the solution after defined time (c_t, mmol/L) using the following equation:

$$q = (c_0 - c_t) \cdot \frac{V}{m}\,[\text{mmol/g}]$$

where V is the solution volume (L) and m is the weight of sorbent material (g). The total uptake capacity of metal ions presents the metal ion uptake at equilibrium.

Sorption efficiency: Sorption efficiency (SE, %) was defined as the quotient of the final concentration of metal ions in the solution after defined time (c_t, mmol/L) and the initial concentration of metal ions in solution (c_0, mmol/L):

$$\text{SE} = \frac{c_t}{c_0} \cdot 100\,[\%]$$

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