Metals in aqueous solutions and real effluents: Biosorption behavior onto a hemp-based felt

(Short title: Metal removal by a hemp-based felt)

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This paper is dedicated to the memory of Peter Winterton.

ABSTRACT

BACKGROUND: In this study, a hemp-based material in the form of a felt is used to adsorb metals in individual aqueous solutions and in polycontaminated effluents using the batch method. The factors affecting the biosorption process were initial metal concentration, biosorbent dosage, contact time and pH.

RESULTS: In controlled conditions, results showed that: (i) the felt exhibited high adsorption capacities towards metals in the following order: Pb > Cd > Cu > Zn > Co ~ Fe ~ Ni ~ Cr ~ Al ~ Mn; (ii) no significant differences were observed for the three salts used (sulfate, chloride and nitrate); (iii) the process was rapid: 10 min were sufficient to attain equilibrium; iv) the biosorption efficiency increased considerably with the increase of the biosorbent dosage; and (v) the adsorption capacities were independent of pH between 4 - 6. The maximum adsorption capacities for Cd, Cu, Zn, Co, Fe, Ni, Cr, Al and Mn were 27.47, 14.64, 10.59, 7.99, 7.85, 7.87, 6.53, 6.38 and 4.55 mg/g, respectively. Interesting results were also obtained for real polymetallic effluents. Ecotoxicological tests also confirmed the efficiency of the biosorption to radically decrease the effluent toxicity.

CONCLUSIONS: Based on these results, hemp-based felt could serve as a novel and efficient biosorbent material for pollutant removal from industrial effluents.

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1. Introduction

The chemical contamination of water by a wide range of metals is a serious environmental problem involving potential human toxicity. Therefore, there is a need to develop technologies that can remove toxic substances including metals from wastewaters. Biosorption using non-conventional natural materials has been proposed as an economical and effective method to adsorb metals present in aqueous solutions at trace levels over traditional treatment methods such as membrane filtration, evaporation, adsorption onto activated carbons, and ion-exchange or chelation using organic resins.[1-9]

An important class of new materials is based on the use of hemp, an annual high yielding industrial crop grown for its fibers and seeds. Hemp is an interesting raw material because of its low-cost, readily availability, particular chemical composition of its fibres, mainly cellulose (over 75%), and for its versatility.[10] Applications are found in numerous sectors of industry, including pulp and paper, textiles, construction, automotive applications, composites (plastic, packaging), agrochemistry, food-chemistry, cosmetics and essential oils, pharmacy and medicine, adhesives and biotechnology. In recent years, hemp-based materials have been proposed for metal ion removal from aqueous synthetic solutions. Abundant data on this topic can be found in the literature.[11-19] However, these published works focus on the removal of metals present in synthetic solutions using hemp in fibre form.

In this study, we propose the use of a hemp-based material in the form of felt to treat metals present in monometallic aqueous solutions or in polycontaminated effluents. The metal studied are: Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. They are chosen for two reasons: firstly these metals (except Cd) are studied due to their common presence in discharge waters from the metal industry, and secondly, six metals (Cd, Cu, Cr, Ni, Pb and Zn) are included in the list of priority pollutants defined by the French Water Agency (French Circular, July 27, 2015). Here different controlling experimental conditions are investigated and discussed. The main parameters studied were initial metal concentration, effect of counter-ions (sulfate, nitrate and chloride metallic salts) biosorbent dosage, contact time and pH. We also report the performance of hemp-based felt to treat a mixture of metals present in industrial effluents.

2. Material and methods

2.1. Material

The hemp-based material was provided by the French company Eurochanvre (Haute-Saône, France). The hemp felt was made of 100% fibre. Its characteristics are reported in Table 1. Before use, the material was extensively washed in reverse osmosis (RO) water (pH = 5.0 ± 0.1) and then dried at 60°C to constant weight.[20]

Table 1

2.2. Metals

$Al_2(SO_4)_3.16H_2O$, $CdSO_4.8H_2O$, $CdCl_2$, $CoSO_4.7H_2O$, $CoCl_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $CrK(SO_4)_2.12H_2O$, $CuSO_4.5H_2O$, $CuCl_2.2H_2O$, $FeSO_4$, $MnSO_4.4H_2O$, $MnCl_2.2H_2O$, $NiSO_4.6H_2O$, $NiCl_2.6H_2O$, $Ni(NO_3)_2$, $PbSO_4$, and $ZnSO_4.7H_2O$ were purchased from Sigma-Aldrich (France) and used without further purification. Appropriate weights of each metal were dissolved in RO water to obtain a stock solution containing about 300 mg/L (except for Pb for which the concentration of the stock solution was 25 mg/L due to its poor solubility). Solutions at lower concentrations (1, 10, 25, 50, 100, 150 and 200) were obtained by dilution of the stock solution. All the solutions were analyzed prior to each experiment.

2.3. Biosorption of metals by batch technique

Metal removal from solutions (spiked solutions or real effluents) by biosorption on hemp materials was studied by a batch method without changing the initial pH of the solution (pH = 5.0 ± 0.1). In each experiment, a fixed mass of felt was introduced into a given metal solution (100 mL) at a known concentration (for spiked solutions) in a tightly closed flask. The mixture was then mechanically stirred for a given time on a rotating shaker at constant speed (250 rpm) and at room temperature (21 ± 1°C). After treatment, the hemp felt was then easily removed and the concentration of the solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ThermoFisher, iCAP 6500, Courtaboeuf, France). The biosorption performance was finally calculated and expressed as percentage abatement (%R). In controlled conditions, initial metal concentration (1, 10, 25, 50, 100, 150, 200 and 300 mg/L) in the solution, biosorbent dosage (0.25, 0.5, 1, 1.5 and 2 g) and pH solution (between 1 - 6) were varied to investigate their effect on the biosorption capacity. Studies were also conducted for various time intervals (ranging from 1 - 60 min) to determine when biosorption equilibrium was reached. All experiments (controlled conditions or real effluents)

were run in triplicate and found reproducible (experimental error within 3%). Blanks were run without any material to determine the extent of metal removal by containers (no adsorption was observed). It was noted that, at the end of the biosorption process, a slight pH variation of between 0.5 and 0.8 units and between 0.6 and 0.7 units was observed for spiked solutions and real effluents in each experiment, respectively.

2.4. Analytical methods

Pollutants were assayed by a certified laboratory following a standard protocol and analyzed by ICP-AES[21] and results expressed in mg/L. When the concentrations were lower than the quantification limits (QL) or the detection limits (DL), the values of these limits were taken into account to calculate the percentage abatement. The pH was measured using a portable pH-meter (model 3110 WTW, Alès, France).

To evaluate changes in the surface morphology of the biosorbent, scanning electron microscopy images (ESEM FEI Quanta 450) with a tungsten filament voltage from 15 keV to 20 keV and low-vacuum conditions were performed. Elemental analysis of the fibre surfaces was also performed using a probe for energy-dispersive X-ray spectroscopy (EDS) and electron beam excitation (with a voltage from 15 keV to 20 keV).

2.5. Industrial effluents

Eight industrial effluents (abbreviated RE for real effluents) were collected for two sampling campaigns (four samples for each campaign taken on four consecutive days, representative samples of a daily activity) from the VMC Pêche metal-finishing factory located in Morvillars (Territoire de Belfort, France). This factory specializes in hook design and production and uses large volumes of water and chemical products, generating volumes of raw effluents about ~40 m^3 per day, processed by a physicochemical treatment. This involves several successive steps (coagulation, precipitation, electrocoagulation, flocculation, settling and filtration). The characteristics of eight RE (collected after the first precipitation) are shown in Table 2. The values (mg/L) described in this table represent the minimal and maximal concentrations obtained for the 8 effluents studied. For this industry, discharge standards should be: Fe <5 mg/L; Al 5 mg/L; Zn 2 mg/L, Ni 1 mg/L; Cr 0.5 mg/L, and Cu 0.5 mg/L.

Table 2

2.6. Ecotoxicological tests

To determine the toxicity of the effluents, a standardized bioassay based on the mobility of *Daphnia magna* was used.[22] The toxicity of five samples before and after treatment were studied. Their values were expressed by the EC50, effective concentration corresponding to 50% inhibition compared to controls (given in percentage of effluent).

3. Results and discussion

3.1. Effect of initial metal concentration

First, to study the effect of the initial metal concentration on biosorption performance, a series of freshly prepared metal ion solutions was used (solutions prepared with metal sulfate salts). Figure 1 shows the influence of initial metal concentration on the removal of 10 metals in mono-component system (concentrations of 1, 10, 25, 50, 100, 150, 200 and 300 mg/L for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn, and only 1, 10 and 25 mg/L for Pb due to its poor solubility). The volume of solution, biosorbent dose and the contact time used in these experiments were 100 mL, 1 g and 60 min, respectively. The results described in Figure 1 show that, up to 25 mg/L, hemp exhibited interesting adsorption capacities (R > 60%) with the following affinity: Pb > Cd > Cu > Zn > Co ~ Ni ~ Fe ~ Cr ~ Al ~ Mn. At 25 mg/L, the abatement values for Pb, Cd, Cu, Zn, Co, Ni, Fe, Cr, Al and Mn were 96, 88, 84.5, 77, 70, 68, 67, 67, 66 and 63, respectively. As expected, when the metal concentration was increased, biosorption efficiency decreased, due to the saturation of the biosorption sites on the material. For example, for Cd and Cu, when the initial metal concentration was increased from 10 - 300 mg/L, the removal decreased from 96 to 35% and 91 to 24%, respectively.

From Figure 1, at any concentration, the same order of abatement was obtained for all metals studied, so, the affinity was independent of metal concentration. For the concentration range studied (50 - 300 mg/L), Cd showed the highest affinity (between 80% and 35%) whereas Mn demonstrated the lowest level of removal (between 48 and 13%). Cu also showed interesting affinities (between 78 and 24%). The difference in the degree of adsorption may be attributed to the physical and chemical characteristics of each metal such as ionic radius, electronegativity and molar mass (Table 3). The ionic radii, molar mass and Allred-Rochow electronegativities decrease in the order Pb > Cd > Mn > Zn ~ Fe > Cu ~ Co > Ni > Cr > Al; Pb > Cd > Zn > Cu > Ni ~ Co > Fe > Mn > Cr > Al, and Cu ~ Ni ~ Co > Fe ~ Mn ~ Zn > Cr ~ Pb > Cd ~ Al, respectively. However, the two largest ions, lead and cadmium, for which

affinities were high, indicated that the size of ions, the molar mass and the electronegativity were not the only determining parameter in the adsorption process. Similar conclusions were reached by Pejić et al.[16,17] and Kyzas et al.[19].

Table 3

Figure 1.

3.2. Effect of counter-ions on metal biosorption

The effect of counter-ions in a biosorption system is an important issue as real effluents can contain anions other than sulfate, such as nitrate and chloride. The effect of counter-ions on the biosorption of Ni and Co by hemp is represented in Figure 2. For these two metals no significant differences in the abatement were observed for the three salts used (sulfate, chloride and nitrate). Similar results were obtained for other metals.

Figure 2.

3.3. Effect of biosorbent dose

Metal biosorption on hemp material was studied by changing the amount of biosorbent (0.25, 0.5, 1, 1.5, and 2 g) added to sample at different initial metal concentrations (25, 50, 100, 150, 200 and 300 mg/L) while maintaining the volume (100 mL), the contact time (60 min) and the agitation speed (250 rpm) constant. The results (Figure 3) showed that metal removal increased with the mass of biosorbent reaching equilibrium between 1 g (for Cd, Cu and Pb) and 1.5 g (for Zn, Ni, Co, Mn, Fe, Cr, Al) of added material. As expected, this overall trend corresponds to the increase of the interactions between biosorbing material and metals, due to the higher biosorbent surface area, and thus the available active sites.

Figure 3.

3.4. Effect of contact time

Biosorption of the metal ions on hemp was studied over a range of time (1-60 min) and three concentrations (5, 25 and 100 mg/L) whilst maintaining other parameters constant. The plots (Figure 4) representing the metal abatement can be split in three distinct regions: the first indicates instantaneous biosorption of the metal within 5 min of contact time suggesting rapid surface adsorption and external diffusion; the second shows a gradual equilibrium (between 5 - 10 min) and the third (after 10 min) indicates the equilibrium state. The kinetics of biosorption were fast and independent of the metal concentration with equilibrium reached in

10 min for all metals. It is also interesting to note that the plots are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of metal on the surface of the biosorbent, and this could confirm the applicability of the Langmuir model.

Indeed, interactions involved were analyzed through classical kinetic and equilibrium models used in the literature. The experimental data suit pseudo-second order kinetics with three biosorption stages (data not published). The Langmuir equilibrium model predicted the following maximum capacities (q_{max} mg/g) of 27.47, 14.64, 10.59, 7.99, 7.85, 7.87, 6.53, 6.38 and 4.55 mg/g biosorbent for Cd, Cu, Zn, Co, Fe, Ni, Cr, Al and Mn, respectively. A direct comparison of literature data using different hemp materials is not possible since both biosorbents and experimental conditions are different. Nevertheless, it was observed that the q_{max} values of the proposed biosorbent were comparable to those of the other available hemp-based materials for metal removal (Table 4).

Figure 4.

Table 4

3.5. Effect of pH

The effect of solution pH on metal abatement was studied by varying the initial pH between 1 - 6, keeping the other parameters constant. The pH behavior of all metals was similar (Figure 5). The percentage removal was strongly pH-dependent in the pH range 1-4 whereas the performances were independent between pH 4 and 6. At pH lower than 3, the abatements decreased drastically due to the competition of H^+, except for Pb and Cu. A similar trend was reported for the adsorption of Ag, Cd, Co, and Zn by hemp fibres by Păduraru and Tofan[12], Tofan et al.[13,14], Pejić et al.[16,17], and Rezić.[18]

Figure 5.

3.6. Elimination and regeneration

Like all agricultural materials, after biosorption the felt as a low cost material can be incinerated to a much smaller volume of ash and/or recovery of biosorbed metal.[23] Regeneration is another solution: since the interactions between the metal and material were driven by weak interactions, acidic solutions can be used for the regeneration. Thus using a 0.1 mol/L HCl solution, the material was easily regenerated. After several adsorption-regeneration cycles (n = 5), the performance remained unchanged, showing the good reproducibility of the data.

3.7. Test with real effluents

Table 3 reported the minimal and maximal values obtained during the two campaigns of sampling. For each campaign, four effluents, each representative of a whole day's activity of the plant, were sampled on 4 consecutive days. The pH values of the effluents were found to be relatively stable at around pH = 4.9 ± 0.1, which was the mean value for eight samples. Analytical monitoring of these effluents showed that 14 metals were found at least once: Al, Cd, Co, Cu, Cr, Fe, Li, Mn, Ni, Pb, Sn, Sr, Ti, and Zn. Of the 14 metals founds, 8 systematically occurred at detectable levels, i.e. Al, Co, Cu, Cr, Fe, Mn, Ni and Zn. Other metals such as Ag, As, Ba, Hg, Mo, Pd, Pt, Sb, Se, Tl, V, and W were below the QL. Eight other substances were identified and quantified for the two campaigns: Ca, K, Mg, Na, P, S, Si, and B. These results demonstrated that real effluents contained a high inorganic load. It is also important to note that the metal load was quantitatively variable (Table 3).

The concentrations of the substances obtained after treatment by biosorption are presented in Table 5. These results demonstrated that high levels of metal removal were attained with the use of hemp, allowing water quality criteria regarding industrial discharge waters to be achieved. This treatment led to the almost total elimination of metals such as Cd, Pb, Cu, and Ni. The treatment also lowered Fe, Zn, Co, Cr, Al, and Mn (campaign 1) by more than 85%, 84%, 69%, 68%, 43% and 26%, respectively. Certain substances such as Na, P, S and B were also eliminated by the process.

The performances of the based-hemp material toward pollutants present in real effluents can be explained by the presence of interactions between the metallic ions and the felt through physisorption (surface adsorption) and chemisorption (electrostatic interactions, precipitation) mechanisms. [12,16,19,23-27] It was noted that, at the end of the biosorption process, a slight pH variation between 0.6 and 0.7 units was observed in each experiment, indicating a chemisorption mechanism. To confirm this and to evaluate changes in the surface morphology of the biosorbent, SEM images and elemental analysis using EDS were performed.[24] The SEM images indicated changes in the morphology of hemp after biosorption (Figure 6). SEM and EDS studies of raw and loaded biosorbent also confirmed the involvement of precipitation in the biosorption process. After biosorption, three of the ten metals (*i.e.* Al, Fe, and Zn) systematically encountered in the effluents and all the other substances except B (*i.e.* Ca, K, Mg, Na, P, S, Si) were detected using EDS at the surface of the fibres constituting the felt. In particular, it is interesting to note also the presence, in the EDS spectra (Figure 6c), of

agglomerate make up of S, a substance present in real effluents. Thus the felt was also useful to eliminate substances other than metals.

Table 5

Figure 6.

3.8. Ecotoxicological analysis of raw and treated effluents

Toxicity tests were carried out by applying a standard test to discharged industrial effluents and to the same discharged waters after biosorption treatment. The toxicity values of five effluents described in Table 6 showed that effluents were relatively toxic for *Daphnia magna*. EC50 values ranged from 5 for sample E2 to 44 for sample E3. According to a French guide on the use of bioassays for the quality assessment of environmental samples[4,22], the effluents were classified between toxic (EC50 < 50%) and very toxic (EC50 < 10%). After biosorption, the impact on *D. magna* was reduced indicated by higher EC values (Table 6). Thus removal of pollutants by the treatment obviously decreased the water toxicity. More experiments are in progress to confirm these chemical and biological results.

Table 6.

4. Conclusion

In this study, the potential of a hemp-based felt for biosorption of metals from aqueous solutions and real effluents was explored in a batch system. In controlled conditions, the effect of process parameters such as biosorbent dose, metal concentration, contact time and pH was examined. The optimum values for biosorbent dosage, contact time and pH for metal biosorption were 1.5 g, 10 min and 5, respectively. High adsorption capacities were found using these conditions. The maximum adsorption capacities for Cd, Cu, Zn, Co, Fe, Ni, Cr, Al and Mn were 27.47, 14.64, 10.59, 7.99, 7.85, 7.87, 6.53, 6.38 and 4.55 mg/g of hemp, respectively. Good results were also obtained for real polymetallic effluents containing concentrations ranging from: Fe 6.9 to 24.5 mg/L; Ni 5.55 to 14.3 mg/L; Zn 3.3 to 11.6 mg/L; Al 1.1 to 9.6 mg/L; Cu 0.43 to 5.5 mg/L, and Cr 0.35 to 2.1 mg/L. The hemp was able to remove, in most cases 75-80% of metal load, allowing water quality criteria regarding industrial discharge waters containing these six metals to be achieved. Ecotoxicological tests also confirmed the efficiency of the biosorption to radically decrease the effluent toxicity. The study of the interactions involved in the biosorption process was studied by employing SEM

and EDS techniques which revealed that both surface interactions and precipitation participate in metal removal from aqueous solutions. The next step will consist of carrying out a semi-industrial scale test to investigate the feasibility of its implementation on an industrial scale.

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Tables

Table 1
Characteristics of hemp-based material.

Thick	about 5 mm
Cellulose	75%
Hemicellulose	15%
Lignin	3%
Pectins	5%
%C	41.4
%N	0.28
%S	0.06

Table 2
Minima and maxima (± standard deviation) for several pollutants over four real effluents (RE) during the two sampling campaigns (four samples taken on four consecutive days, representative samples of a daily activity; the results are expressed in concentration in mg/L; pH measured at 20°C).

Parameter / Pollutant	Campaign 1	Campaign 2
Samples	**RE1, RE2 RE3, RE4**	**RE5, RE6 RE7, RE8**
pH	4.7-5.1 (0.2)	4.6-5.1 (0.2)
Al	1.99-9.6 (3.5)	1.1-3.74 (1)
Cd	<QL-0.25 (0.1)	<QL-0.16 (0.07)
Co	3.36-7.55 (2.4)	7.3-13.34 (2.3)
Cr	0.35-2.1 (0.8)	0.45-0.74 (0.1)
Cu	0.97-5.5 (2.3)	0.43-1.61 (0.4)
Fe	8.7-24.5 (7.6)	6.9-14.4 (3)
Mn	4.8-22.3 (8.3)	3.99-10.1 (2.6)
Ni	5.55-14.3 (4.1)	5.99-8.1 (0.8)
Pb	<QL-0.11 (0.05)	<QL-0.019 (0.02)
Zn	5.9-11.6 (2.6)	3.3-9.1 (2.2)
Li	<QL-0.52 (0.27)	<QL-0.1 (0.04)
Sn	<QL-1.95 (1.02)	0.17-0.37 (0.08)
Sr	<QL-0.91 (0.41)	<QL-0.74 (0.27)
Ti	0.44-3.25 (1.2)	<QL-0.47 (0.21)
Ca	438-610 (89)	295-457 (57)
K	22.7-44.6 (9.5)	19.7-34.3 (5.9)
Mg	85-210 (64)	75-132 (22)
Na	260-460 (104)	163-209 (16.7)
P	2.98-7.91 (2.5)	1-1.97 (0.4)
S	9.15-40.5 (12.9)	7.88-29.4 (7.9)
Si	7.88-31.2 (10.2)	8.5-13.7 (1.9)
B	21.2-105 (34.9)	21.2-40 (7.8)

Table 3

Metal ion characteristics.

	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)	Co(II)	Fe(II)	Cr(III)	Al(III)	Mn(II)
Allred-Rochow EN[1]	1.55	1.49	1.75	1.66	1.75	1.7	1.64	1.56	1.47	1.6
MW[2]	207.2	112.4	63.5	65.3	58.7	58.9	55.85	51.99	26.9	54.9
Ionic radius[3]	120	97	72	74	69	72	74	63	51	80

[1] Allred-Rochow electronegativity
[2] molar mass in g/mol
[3] in pm

Table 4

Adsorption capacities (q_{max} in mg/g) for various metals using hemp.

Metal	**Type of biosorbent**	**q_{max}**	**Reference**
Al	Felt	6.38	this study
Cd	Felt	27.47	this study
Cd	Fibres	2.5909	[11]
Co	Fibres	13.58	[13]
Co	Felt	7.99	this study
Cr	Felt	6.53	this study
Cr	Fibres	4.006	[12]
Cu	Felt	14.64	this study
Cu	Fibres	9.0735	[12]
Cu	Shives	3.91	[25]
Fe	Felt	7.87	this study
Mn	Felt	4.55	this study
Ni	Fibres	206	[19]
Ni	Shives	160	[19]
Ni	Felt	7.85	this study
Pb	Fibres	25.05	[13]
Zn	Fibres	21.047	[12]
Zn	Felt	10.59	this study

Table 5
Comparisons of the level of several pollutants present in the industrial effluents before (raw effluents) and after treatment (treated effluents) by biosorption on hemp (the results are expressed as a concentration range deviation minima and maxima (± standard deviation) and as a % mean abatement ± standard deviation for the 4 samples of the two campaigns; the concentrations are expressed in mg/L; pH measured at 20°C).

	Campaign 1			Campaign 2		
Samples	**raw**	**treated**		**raw**	**treated**	
Parameter / Pollutant	**concentration**	**concentration**	**abatement**	**concentration**	**concentration**	**abatement**
pH	4.7-5.1 (0.2)	5.3-5.8 (0.2)		4.6-5.1 (0.2)	5.2-5.8 (0.3)	
Al	1.99-9.6 (3.5)	1.25-4.87 (1.7)	43±5	1.1-3.74 (1)	0.6-2.12 (1)	49±7
Cd	<QL-0.25 (0.1)	<QL	100	<QL-0.16 (0.07)	<QL	100
Co	3.36-7.55 (2.4)	0.8-3.36 (1.1)	69±6	7.3-13.34 (2.3)	2.17-5.01 (1.3)	64±5
Cr	0.35-2.1 (0.8)	0.096-0.58 (0.3)	68±6	0.45-0.74 (0.1)	0.13-0.21 (0.1)	72±2
Cu	0.97-5.5 (2.3)	0.035-0.51 (0.2)	92±3	0.43-1.61 (0.4)	0.02-0.24 (0.1)	92±4
Fe	8.7-24.5 (7.6)	1.01-4.66 (71.8)	85±3	6.9-14.4 (3)	0.71-1.36 (0.3)	89±1
Mn	4.8-22.3 (8.3)	3.14-17.9 (6.9)	26±7	3.99-10.1 (2.6)	0.31-0.52 (0.1)	23±10
Ni	5.55-14.3 (4.1)	0.41-0.74 (0.1)	93±1	5.99-8.1 (0.8)	0.31-0.52 (0.1)	94±1
Pb	<QL-0.11 (0.05)	<QL-0.021 (0.01)	94±11	<QL-0.019 (0.02)	<QL	100
Zn	5.9-11.6 (2.6)	0.78-1.81 (0.5)	86±1	3.3-9.1 (2.2)	0.57-1.97 (0.61)	84±5
Li	<QL-0.52 (0.27)	<QL-0.09 (0.01)	78±6	<QL-0.1 (0.04)	<QL	100
Sn	<QL-1.95 (1.02)	<QL-1.54 (0.8)	21±2	0.17-0.37 (0.08)	0.11-0.3 (0.08)	20±11
Sr	<QL-0.91 (0.41)	<QL-0.66 (0.2)	41±12	<QL-0.74 (0.27)	<QL-0.33 (0.09)	37±18
Ti	0.44-3.25 (1.2)	0.21-1 (0.5)	61±13	<QL-0.47 (0.21)	<QL-0.2 (0.01)	41±15
Ca	438-610 (89)	409-557 (79)	8±1	295-457 (57)	280-420 (57.3)	7±1
K	22.7-44.6 (9.5)	22-43.9 (9.5)	2±1	19.7-34.3 (5.9)	18.9-33.7 (6.7)	4±1
Mg	85-210 (64)	80-201 (61)	5±1	75-132 (22)	72-130 (25.9)	4±2
Na	260-460 (104)	175-370 (102)	24±7	163-209 (16.7)	100-150 (22.5)	30±9
P	2.98-7.91 (2.5)	1.35-4.11 (1.3)	47±10	1-1.97 (0.4)	0.22-0.77 (0.25)	65±9
S	9.15-40.5 (12.9)	6.7-31.2 (10.2)	25±2	7.88-29.4 (7.9)	5.35-22.4 (7.3)	30±4
Si	7.88-31.2 (10.2)	7.44-28.9 (9.4)	7±1	8.5-13.7 (1.9)	7.78-12.4 (1.9)	7±3
B	21.2-105 (34.9)	24.9-90 (30.5)	18±4	21.2-40 (7.8)	11.8-31.6 (9.4)	33±11

Table 6. Total of metals present in solution (in mg/L) before and after biosorption on hemp and toxicity values (expressed by EC50 in percentage of effluent) for *Daphnia magna* for five samples.

Sample	**Total of metals* present in solution in mg/L**		**EC50 in percentage of effluent**	
	raw effluent	**treated effluent**	**raw effluent**	**treated effluent**
E1	44.51	13.69	31	70
E2	98.93	35	5	44
E3	37.7	9.74	44	>90
E4	86.68	32.21	10	51
E5	39.8	9.46	23	71

* Al+Cd+Co+Cr+Cu+Fe+Mn+Ni+Pb+Zn+Li+Sn+Sr+Ti

Figure - Legends

Figure 1. Effect of initial metal concentration on metal removal (expressed in % removal) onto hemp-based felt (solutions prepared with metal sulfate salts; conditions: biosorbent dose 1 g, volume of solution 100 mL, contact time 60 min, agitation speed 250 rpm, pH = 5, temperature 20°C, and n = 3).

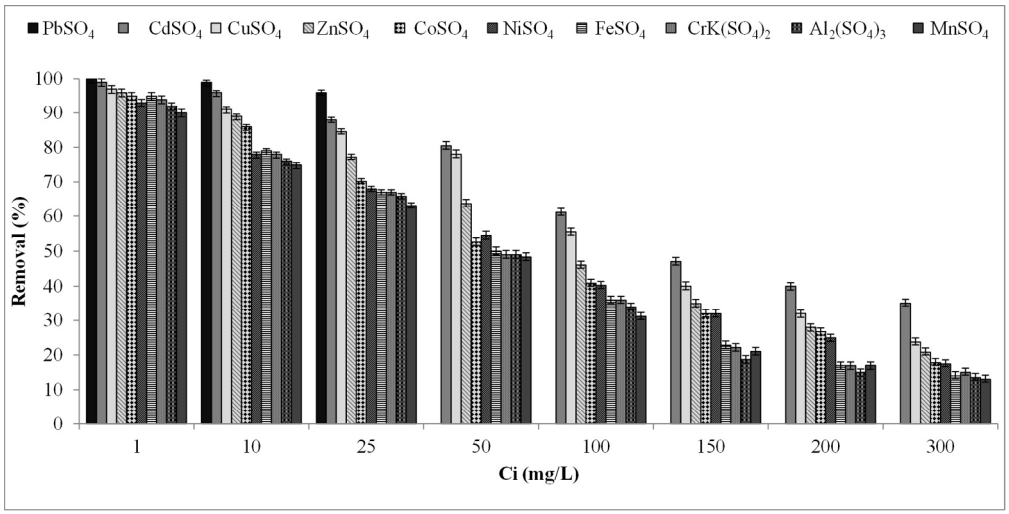
Figure 2. Effect of counter-ions on biosorption of Ni and Co ions (expressed in % removal) by hemp-based felt using different metal salts (conditions: biosorbent dose = 1 g, volume of solution = 100 mL, contact time = 60 min, agitation speed = 250 rpm, pH = 5, temperature = 20°C, and n = 3).

Figure 3. Removal (%) vs. hemp dose at different initial metal concentrations (others conditions: volume of solution 100 mL, contact time 60 min, agitation speed 250 rpm, temperature 20°C, pH = 5, and n = 3).

Figure 4. Kinetics of metal removal (%) by hemp at three different initial metal concentrations (others conditions: adsorbent dose 1 g, volume of solution 100 mL, agitation speed 250 rpm, temperature 20°C, pH = 5, and n = 3).

Figure 5. Influence of pH on the abatement of ten metals (expressed in % removal) by hemp (conditions: adsorbent 1 g, volume of the solution 100 mL, initial metal concentration 25 mg/L).

Figure 6. SEM images (left) and EDS (right) spectra of the felt before (a) and after (b,c) biosorption. The red arrow on the SEM image (c) shows agglomerates at the surface of the fibre.



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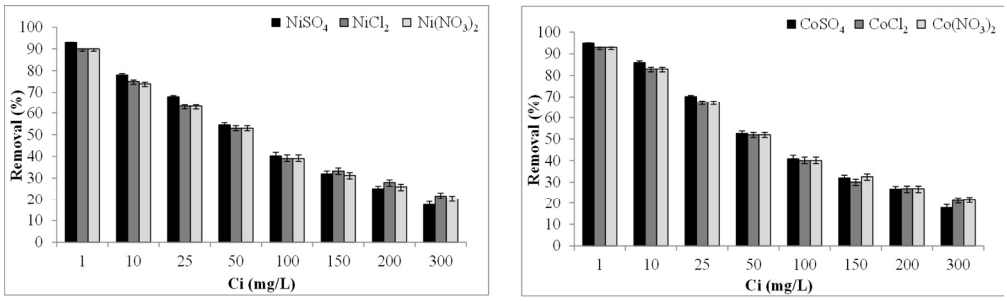


Figure 2. Effect of counter-ions on biosorption of Ni and Co ions (expressed in % removal) by hemp-based felt using different metal salts (conditions: biosorbent dose = 1 g, volume of solution = 100 mL, contact time = 60 min, agitation speed = 250 rpm, pH = 5, temperature = 20°C, and n = 3).

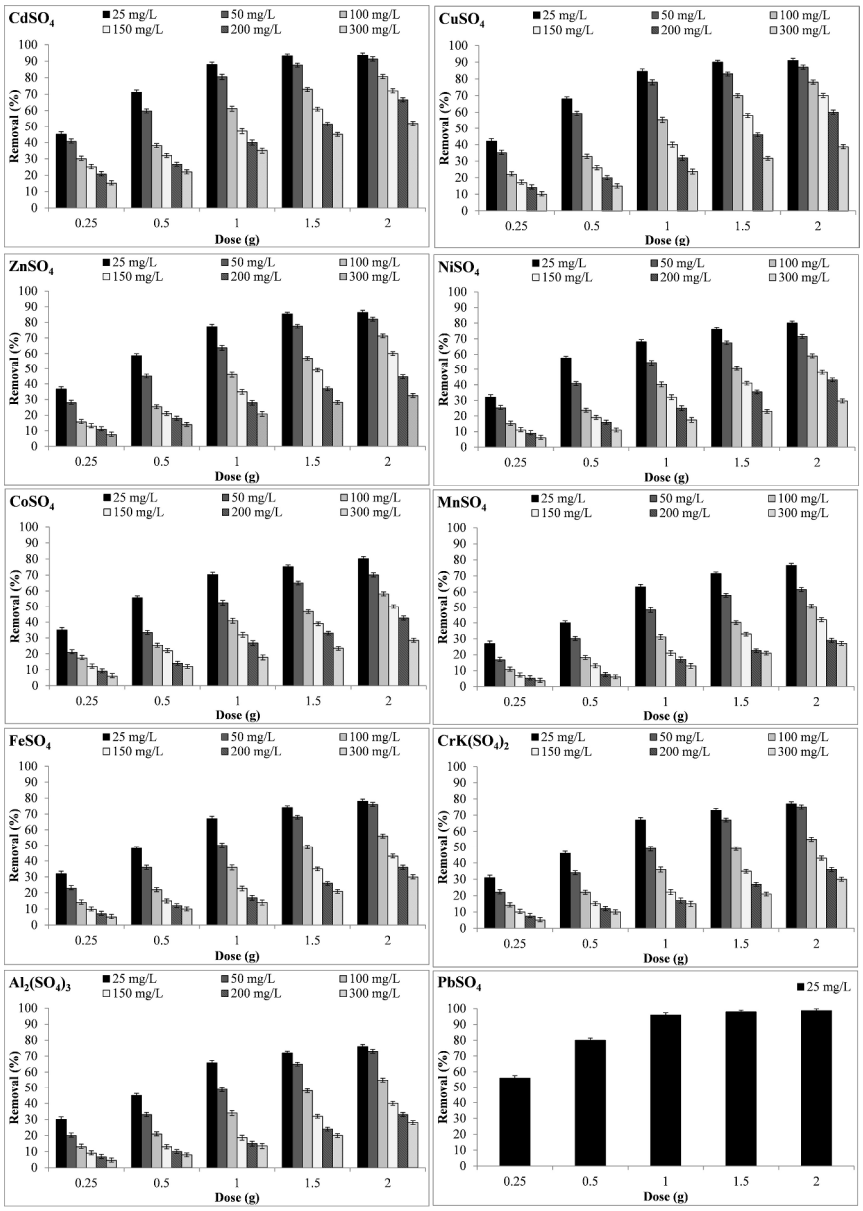


Figure 3. Removal (%) vs. hemp dose at different initial metal concentrations (others conditions: volume of solution 100 mL, contact time 60 min, agitation speed 250 rpm, temperature 20°C, pH = 5, and n = 3).

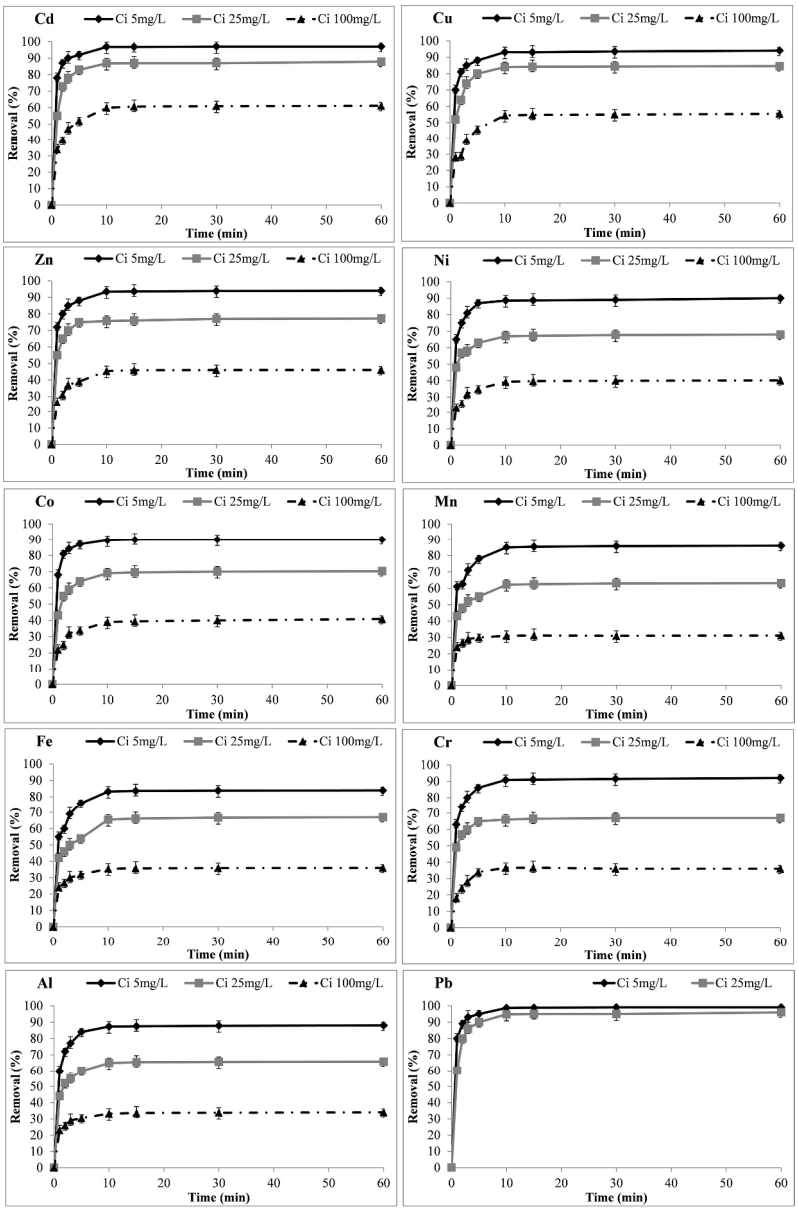


Figure 4. Kinetics of metal removal (%) by hemp at three different initial metal concentrations (others conditions: adsorbent dose 1 g, volume of solution 100 mL, agitation speed 250 rpm, temperature 20°C, pH = 5, and n = 3).

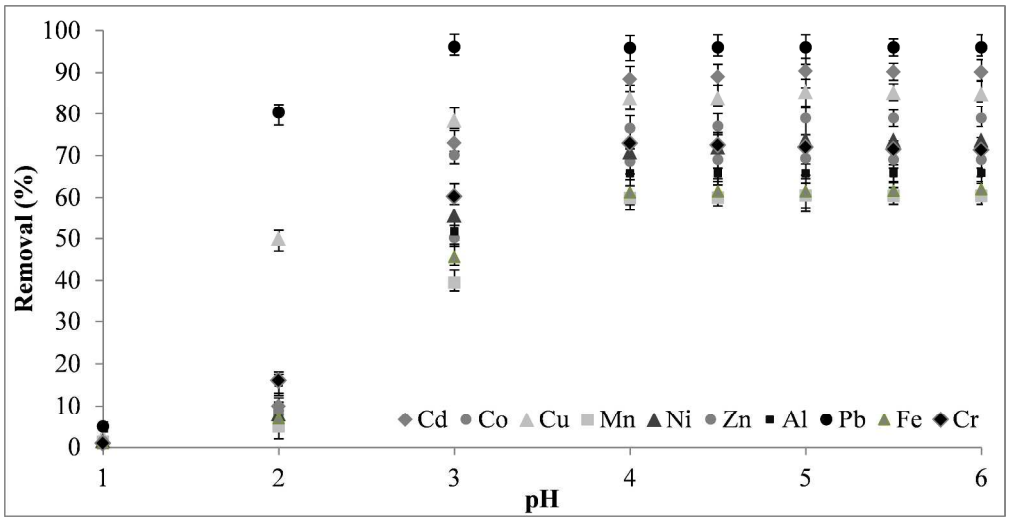
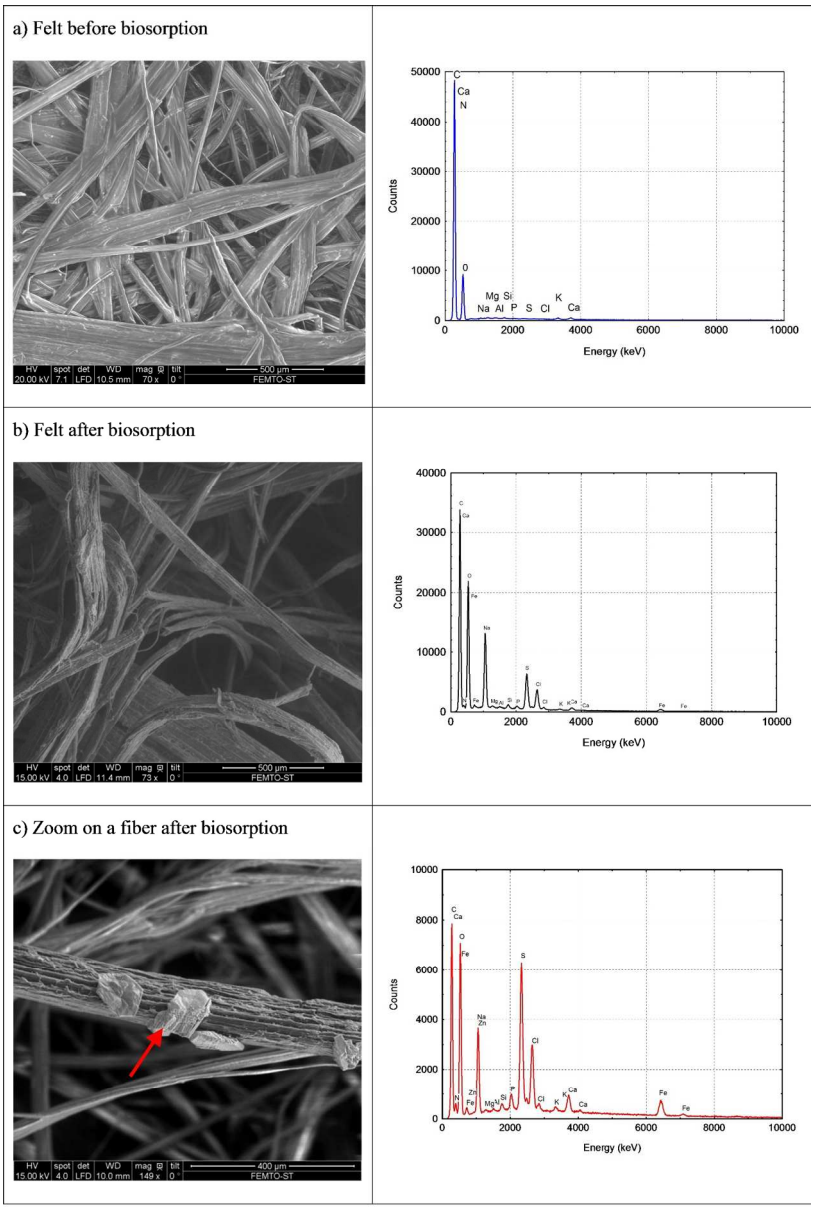


Figure 5. Influence of pH on the abatement of ten metals (expressed in % removal) by hemp (conditions: adsorbent 1 g, volume of the solution 100 mL, initial metal concentration 25 mg/L).



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