Simultaneous Removal of Inorganic and Organic Pollutants from Polycontaminated Wastewaters on Modified Hemp-Based Felts

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Abstract: In this study, an adsorption process using hemp-based materials in felt form was applied to remove between 45 and 53 contaminants present in wastewater from the surface treatment industry. Several materials were compared using batch experiments, including a felt made of 100% hemp fiber (HEMP), the same felt cross-linked with 1,2,3,4-butanetetracarboxylic acid (HEMPBA), a felt coated with a maltodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer (HEMPM), and a felt coated with hydroxypropyl-β-cyclodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer (HEMPCD). Chemical analysis showed that HEMPBA, HEMPM and HEMPCD materials had high adsorption capacities on metals in wastewater, confirming the role of carboxylic groups. Only HEMPCD was able to remove both metals and organics, resulting in the virtual elimination of organics such as chloroform, 1,2-dichlorobenzene, and nonylphenol. This result demonstrated the important role of cyclodextrin molecules in adsorption mechanism. HEMPCD also resulted in an important decrease in residual chemical oxygen demand and total organic carbon of more than 83% and 53%, respectively, while the treatment with HEMP lowered them by 12% and 12%, HEMPBA by 9% and 7%, and HEMPM by 45% and 26%. Chemical abatement and toxicity mitigation have demonstrated that adsorption onto a non-conventional material could be an interesting treatment step for the detoxification of wastewater.

Keywords: hemp, pollutants, wastewater, adsorption, batch experiments, cyclodextrin

1. Introduction

The European policy on water pollution results from the Water Framework Directive (WFD, Directive 2000/60/EC) of 2000, which established guidelines for the protection of surface water, underground water and coastal water in Europe. One of the objectives is to achieve good chemical and ecological status of all water bodies in Europe, before a deadline set for 2021 [1]. The WFD also classified chemicals into two main lists of priority substances (Directive 2006/11/EC). The first concerns particularly dangerous substances such as mercury, anthracene, 4-p-nonylphenol, pentachlorophenol and trichloromethane, substances considered to be highly toxic, persistent and bioaccumulative. The second includes priority substances such as trichlorobenzene, octylphenols, dichloromethane, lead and nickel, which are considered less toxic than those of the first list, but nevertheless present a significant risk to the environment. The surface treatment industry is particularly affected by many of these substances [1-3]. Since the 2000s, Europe is asking industry to innovate to reduce and/or to eliminate chemicals present in their waters, i.e. wastewaters and discharge waters. Although considerable efforts have been made by the industry in general, and surface treatment industry in particular, over the last 20 years, the problem of water pollution remains a significant concern. So, the industrial sector continues to look into new treatment methods to decrease the levels of pollution present in their wastewaters [1,4,5].

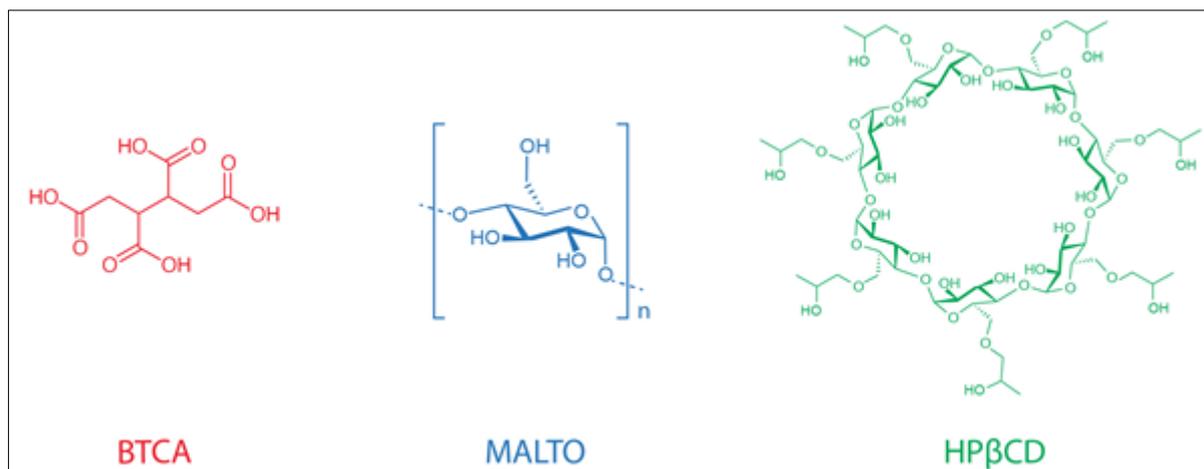**email: gregorio.crini@univ-fcomte.fr*

The recent literature reports a multitude of low-cost, readily available and effective non-conventional agricultural and forestry materials for the treatment of contaminated waters, such as coir, jute, date pits, corncob, fruit peel waste, sawdust and bark [6-13]. Hemp-based materials have also been proposed for the removal of metals, mainly present in synthetic aqueous solutions [14-31]. The Romanian group of Păduraru [14-18], the Serbian group of Kostić [18-20] and the French group of Crini [25-31] are particularly active in this field. Our group recently published the first comprehensive review on metal sequestration by hemp-based adsorbents [30].

In previous works [27,28,31], we first proposed the use of a hemp material in felt form to treat metals present in synthetic polymetallic aqueous solutions and in discharge waters containing a mixture of metals. These discharges contained a relatively low contaminant load, but complied with regulations. Continuing our interest in these materials, we have presented here the results of analytical and ecotoxicological monitoring of wastewaters from a surface treatment industry containing a high contaminant load before and after hemp treatment using raw and modified materials. The two main objectives were to determine the ability of the materials to treat high contaminant loads and to highlight the role of the structure of the material in its performance in removing organic and inorganic contaminants. Four hemp-based materials were compared using batch experiments, a felt made of 100% hemp fiber, the same felt cross-linked with 1,2,3,4-butanetetracarboxylic acid, a felt coated with a maltodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer, and a felt coated with hydroxypropyl-β-cyclodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer [26-29,31]. The chemical modification was made to provide ion-exchange properties to the material by introducing carboxylic groups [32-34]. First, a chemical and ecotoxicological analysis of three wastewaters was performed. Thirteen standard water parameters and over 170 substances including 33 metals, 58 volatile organic compounds (VOCs), 16 polycyclic aromatic compounds (PAHs), 24 chlorophenols (CPs), 16 alkyl-phenols (APs), 5 chloroanilines (CAs), 7 polychlorobiphenyls (PCBs), and 4 organo-tin complexes were monitored. Two ecotoxicological tests, namely measurements of inhibition of *Daphnia magna* mobility and germination rate of *Lactuca sativa* seeds, were also carried out on wastewaters. Then, we compared the performance of the four materials in the removal of the contaminants present in industrial effluents. This article presents the abatements obtained in chemical pollution and the impact on water toxicity before and after hemp treatment.

2. Materials and methods
2.1 Hemp-based materials

Hemp was kindly provided by Eurochanvre, a hemp processing company in Franche-Comté (Arc-les-Gray, Haute-Saône, France). This material, noted HEMP, is a felt made of 100% hemp fiber. Before chemical modification, HEMP was extensively washed with osmosed water and then dried at 60°C until constant weight. Three modified materials were synthetized in order to provide ion-exchange properties to the HEMP material by introducing carboxylic groups through a cross-linking reaction with 1,2,3,4-butanetetracarboxylic acid (BTCA) in absence or in presence of maltodextrin (MALTO, Glucidex® D19 from Roquette, Lestrem, France) or of hydroxypropyl-β-cyclodextrin (HPβCD from Roquette, Lestrem, France). Chemical structures are reported in Scheme 1. The process and associated chemical pathway to produce a felt cross-linked with 1,2,3,4-butanetetracarboxylic acid (HEMPBA), a felt coated with a maltodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer (HEMPM), and a felt coated with hydroxypropyl-β-cyclodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer (HEMPCD) have been detailed elsewhere [26,27,30-34].

Scheme 1. Chemical structure of 1,2,3,4-butanetetracarboxylic acid (BTCA), maltodextrin (MALTO), and hydroxypropyl-β-cyclodextrin (HPβCD)

During the synthesis, a cross-linking reaction occurs by esterification in three possible cases (Scheme 2), depending on the reagents used: (1) a reaction between the BTCA carboxylic groups and the cellulose hydroxyl groups of hemp fibers (synthesis of HEMPBA); (2) an esterification between the BTCA carboxylic groups and the MALTO hydroxyl groups on the one hand, and cellulose hydroxyl groups of hemp fibers on the other hand (HEMPM); and (3) a cross-linking reaction between the BTCA carboxylic groups and the HPβCD hydroxyl groups on the one hand, and cellulose hydroxyl groups of hemp fibers on the other hand (HEMPCD). BTCA undergoes a first dehydration under heating to give a 6-membered cyclic anhydride that reacts easily with a cellulose of MALTO (or HPβCD) anhydroglucose unit, forming a first ester group and returning a free carboxylic group [32-34]. Two remaining free carboxylic groups of esterified BTCA then form a second cyclic anhydride, which also reacts by esterification with cellulose or MALTO (or HPβCD) anhydroglucose units, releasing another free carboxylic acid group. This leads to a cross-linked polysaccharide network rich in carboxylic groups (scheme 2). Table 1 reports the characteristics of the four hemp-based materials used in this work.

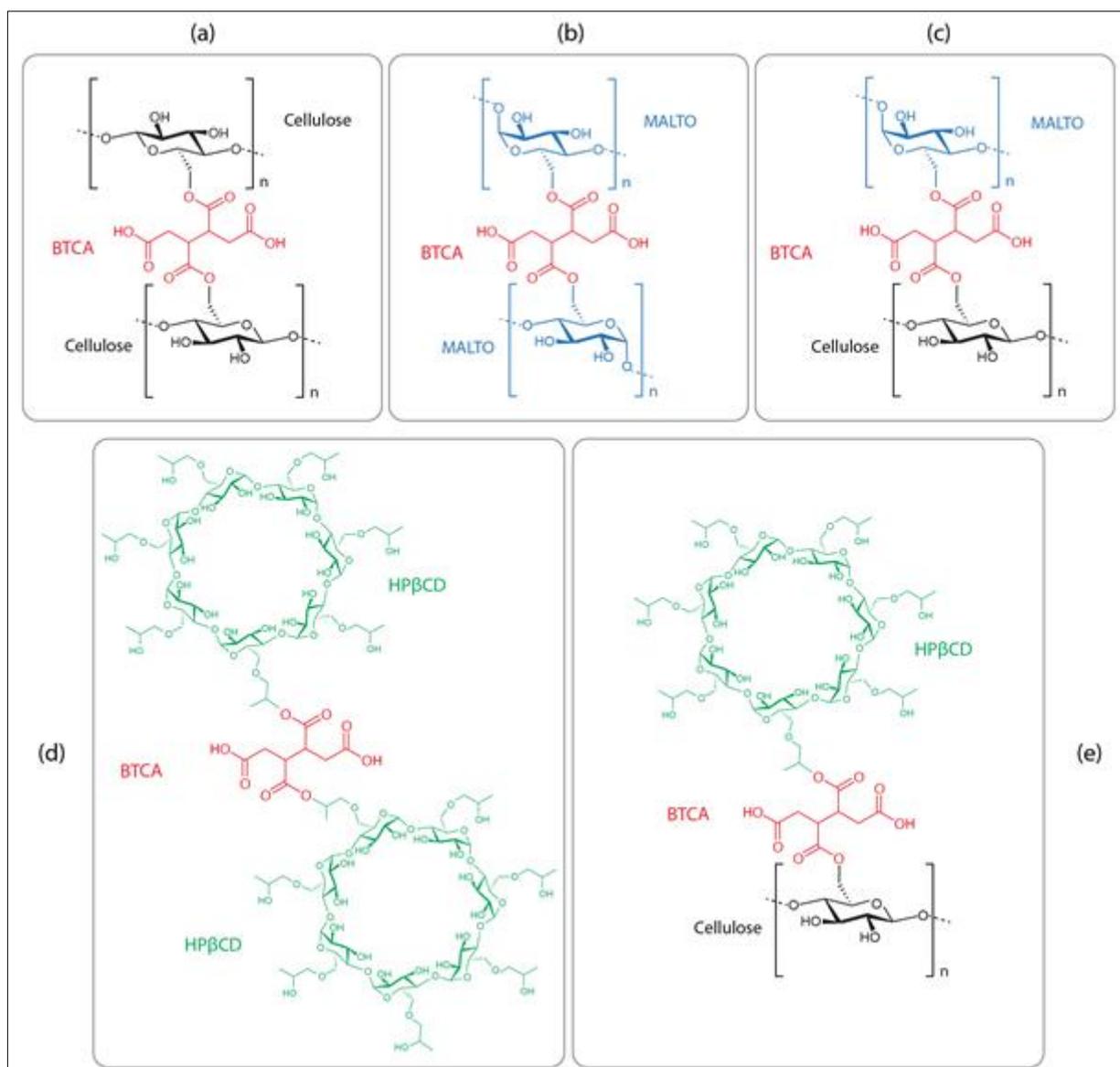**Table 1.** General description and properties of materials

Code	HEMP	HEMPBA	HEMPM	HEMPCD
Raw material	fiber	fiber	fiber	fiber
Form	felt	felt	felt	felt
Cross-linking agent		BTCA[1]	BTCA[1]	BTCA[1]
Matrix			MALTO[2]	HPβCD[3]
Functional group		carboxylate	carboxylate	carboxylate
IEC[4]	0.19 ± 0.09	1.41 ± 0.04	1.08 ± 0.03	1.18 ± 0.16
Ionic form-shipped		Na⁺	Na⁺	Na⁺
%C	42.7	45.9	53.2	55.5
%N	0.33	0.28	0.31	0.32
%S	0.09	0.06	0.07	0.08

[1]1,2,3,4-butanetetracarboxylic acid
[2]Maltodextrin
[3]Hydroxypropyl-β-cyclodextrin
[4]Ion exchange capacity, in meq/g

Scheme 2. Possible reactions between 1,2,3,4-butanetetracarboxylic acid (BTCA) and anhydro glucose units of: a) two cellulose chains; b) two maltodextrins (MALTO), c) one MALTO and one cellulose chain; d) two hydroxypropyl-β-cyclodextrin (HPβCD); and e) one HPβCD and one cellulose chain

2.2 Industrial wastewaters

Three wastewaters taken on three consecutive weeks, noted W1, W2 and W3, were collected from VMC Pêche Company located in Morvillars (Territoire de Belfort, France). This metal-finishing factory is specialized in fishing hook design and production. To treat these effluents, the company uses a physicochemical treatment involving two main stages to achieve the desired contaminant removal: (i) a pretreatment using chemical methods (e.g. specific treatment for reducing CrVI in CrIII) and (ii) neutralization steps using hydrated lime as a precipitant insolubilizing minerals such as metals and fluorides). Then, the treated effluent is flocculated and is finally decanted and filtered before being discharged into the aquatic environment if it complies with the regulatory standards. From a chemical point of view, the main industrial concerns are the COD values and the concentrations of nitrates, Ni, Cu, Zn, total Fe+Al, cyanides, and chloroform. The wastewaters, i.e. raw effluents, from production lines studied in this work were collected before being sent to the treatment plant.

2.3 Analytical methods

Full chemical characterization of the samples was carried out by measuring 13 standard water parameters and over 170 chemical substances. The choice of parameters and substances was determined by the regulatory requirements specifically laid down for the surface treatment industry as stipulated in the French Law of 5 September 2006. The water parameters monitored were: pH, conductivity, suspended solids (SS), chemical oxygen demand (COD), total organic content (TOC), the levels of the different forms of nitrogen (nitrates, nitrites and ammonium nitrogen), cyanides (total and easily released), adsorbable halogenated organic compounds (AOX), free chlorine and hydrocarbon index (HI). To identify the inorganic and organic substances present in each wastewater, we analyzed eight broad family of substances classified as follows (in agreement with the French Water Authority): 46 inorganic substances including 33 metals, 58 volatile organic compounds (VOCs), 16 polycyclic aromatic compounds (PAHs), 24 chlorophenols (CPs), 16 alkylphenols (APs), 5 chloroaniline (CAs), 7 poly-chlorobiphenyls (PCBs) and 4 organo-tin complexes. All the protocols have already been detailed elsewhere [28,31,35,36]. The analytical characteristics of three samples, taken on three consecutive weeks, are shown in Table 2 (water parameters), Table 3 (inorganic contaminants), and Table 4 (organic contaminants).

Table 2. Standard water parameters for three wastewaters noted W1, W2 and W3 (SS: suspended solids, COD: chemical oxygen demand; TOC: total organic content; CN_T: total cyanide; AOX: adsorbable halogenated organic compounds; HI: hydrocarbon index)

Parameter	Unit	QL[1]	W1	W2	W3
pH (20°C)			4.7	5	4.3
conductivity (20°C)	µS/cm		8950	11500	7000
SS	mg/L	2	21	30	15
COD	mg/L	5	850	600	510
TOC	mg/L	0.5	95	88	71
nitrates	mg/L	1	200	230	185
nitrites	mg/L	1	<QL	<QL	<QL
ammonium nitrogen	mg/L	0.05	1.55	2.65	1.1
CN_T	mg/L	0.02	<QL	<QL	<QL
easily released cyanide	mg/L	0.02	<QL	<QL	<QL
free chlorine	µg$_{Cl}$/L	0.02	<QL	<QL	<QL
AOX	µg/L	10	2000	3650	5000
HI	mg/L	0.1	<QL	<QL	<QL

[1]Quantification limit

Table 3. Concentrations of the inorganic substances (16 metals and 12 minerals) present in three wastewaters noted W1, W2 and W3

Parameter	Unit	QL[1]	W1	W2	W3
aluminum	mg/L	0.02	0.94	2.21	4.9
cadmium	mg/L	0.002	0.11	0.088	0.15
cobalt	mg/L	0.003	9.2	2.21	6.5
chromium	mg/L	0.005	1.33	0.25	0.61
copper	mg/L	0.005	10.35	6.69	8.89
iron	mg/L	0.02	350	200	460
manganese	mg/L	0.005	25.3	38.2	18.9
molybdenum	mg/L	0.01	0.36	0.29	0.15
nickel	mg/L	0.01	3.77	5.32	4.89

lead	mg/L	0.002	<QL	0.061	0.075
zinc	mg/L	0.01	10.5	17.3	31.6
lithium	mg/L	0.02	<QL	0.09	0.073
tin	mg/L	0.005	0.051	0.078	0.022
strontium	mg/L	0.02	0.666	0.34	0.51
titane	mg/L	0.01	<QL	0.15	0.209
vanadium	mg/L	0.01	0.035	0.059	0.019
magnesium	mg/L	1	150	95	75
phosphorus	mg/L	0.16	1.15	1.25	1.1
boron	mg/L	0.02	50	41	36.8
sodium	mg/L	1	380	335	440
calcium	mg/L	5	300	270	385
potassium	mg/L	0.5	43.5	31.9	25.4
sulfide	mg/L	2	29.9	33.5	18.5
silicon	mg/L	0.01	20	15	17.5
fluorides	mg/L	0.5	23.5	16.7	18.2
chlorides	mg/L	1	900	1150	1080
bromide	mg/L	1	38	80	55
sulphates	mg/L	2	3100	4250	2890

[1]Quantification limit

Table 4. Concentrations of organic substances (9 VOCs, 10 APs, 7 CPs and 5 PAHs) in three wastewaters noted W1, W2 and W3

Parameter	Unit	QL[1]	W1	W2	W3
chloroform	µg/L	0.5	150	350	200
1,2-dichloroethane	µg/L	0.5	<QL	6.65	2.5
dichloromethane	µg/L	0.5	7.55	5.3	6.05
tetrachloroethylene	µg/L	0.5	<QL	26	<QL
trichloroethylene	µg/L	0.5	1.45	1.26	<QL
nonylphenol	µg/L	0.5	75	350	240
4-tert-octylphenol	µg/L	0.5	<QL	4	<QL
4-tert-butylphenol	µg/L	0.5	<QL	5.1	<QL
nonylphenol monoethoxylate	µg/L	0.1	0.12	0.44	0.3
nonylphenol diethoxylate	µg/L	0.1	1.05	<QL	0.91
nonylphenol monoethoxylate	µg/L	0.1	1.5	0.44	3.66
nonylphenol diethoxylate	µg/L	0.1	<QL	10	<QL
2-methylphenol	µg/L	0.05	0.071	<QL	0.06
3-methylphenol	µg/L	0.05	0.05	0.19	0.11
4-methylphenol	µg/L	0.05	<QL	0.07	<QL
2-chlorophenol	µg/L	0.05	<QL	0.15	0.5
4-chlorophenol	µg/L	0.05	<QL	<QL	1
2,4-dichlorophenol	µg/L	0.05	<QL	0.9	1.2
2,3-dichlorophenol	µg/L	0.05	0.08	<QL	<QL
3,4-chlorophenol	µg/L	0.05	<QL	0.15	<QL
2,4,6-trichlorophenol	µg/L	0.25	3.65	2.1	2.5
1,2-dichlorobenzene	µg/L	0.5	51.6	109	84.2
4-chloro-3-methylphenol	µg/L	0.05	<QL	0.33	0.25
toluene	µg/L	1	18	25	<QL
anthracene	µg/L	0.01	0.15	<QL	0.2

phenanthrene	µg/L	0.01	0.2	0.17	0.19
naphthalene	µg/L	0.01	1.1	0.51	1.55
fluoranthene	µg/L	0.01	<QL	0.15	0.24
pyrene	µg/L	0.01	0.018	<QL	0.01
ethylbenzene	µg/L	0.01	1.45	<QL	<QL
isopropylbenzene	µg/L	0.5	1.1	1	<QL

[1]Quantification limit

2.4. Ecotoxicological methods

To determine the potential toxicity of the wastewaters before and after hemp treatment, two ecotoxicological tests were also carried out [35-38]. The first is a standardized bioassay based of the mobility of *Daphnia magna* according to the "Inhibition Protocol Mobility" described in the standardized biomonitoring test ISO 6341-2012. The toxicity was expressed by the EC50, i.e. effective concentration corresponding to 50% inhibition compared to controls, given in percentage of wastewaters. In France, the French Water Authority, a public organization involved in actions to counter pollution, imposes on certain companies the use of this bioassay to check the ecotoxicity of their treated waters before discharge into the aquatic environment. The second test is based on measurements of the germination rate of *Lactuca sativa* seeds (AFNOR NF X 31-201). The results are expressed in percentage germination, with respect to seeds not exposed to the wastewater (control). Our group previously demonstrated that these phytotoxicity tests were simple, quick and reliable, with the advantage of being inexpensive, and useful to assess the impact of industrial effluents before their discharge [37,38]. The two protocols used to evaluate the potential toxicity of the wastewaters before and after hemp treatment have already been detailed elsewhere [35,36]. The ecotoxicological characteristics of three samples are shown in Table 5.

Table 5. Toxicity values expressed in EC50 (effective concentration corresponding to 50% inhibition compared to controls) in percentage of wastewater for *Daphnia magna* and in % of germination of *Lactuca sativa* (germination rate value for the controls: 95% ± 0.5%) for three wastewaters before hemp treatment (n = 3, ± 0.5%)

Bio-indicator		W1	W2	W3
Daphnia magna[1]	EC50[2]	0.7	3.1	2.7
Lactuca sativa[3]	germination in %	20.1	10.5	15.9

[1]n = 1, [2]EC50 = effective concentration, expressed in percentage of wastewater, [3]n = 3

2.5. Batch experiments

Contaminant removal from wastewater by adsorption on hemp-based materials (HEMP, HEMPBA, HEMPM and HEMPCD) was studied by a batch method without changing the initial *p*H of the raw effluent. In each experiment, 30 g of hemp felt were stirred with 15 L of wastewater for 30 min at a constant stirring rate (250 rpm) and room temperature (20 ± 1°C). These conditions have been determined in preliminary studies [28-31]. After treatment, the felt was then withdrawn and the treated wastewater analyzed. The three samples were treated under identical conditions. When the value of a water parameter or of a substance concentration was lower than the quantification limit (QL), the values of this limit were taken into account to calculate the average values, in agreement with the French Water Authority standards [35].

3. Results and discussions

3.1. Analytical characterization of the wastewaters

The primary aim of this study was to identify and quantify the substances present in industrial wastewaters by measuring 13 standard water parameters and over 170 chemical substances. The analytical characterization of three samples, taken on three consecutive weeks, is presented in Table 2 (water parameters), Table 3 (inorganic contaminants) and Table 4 (organic contaminants). The total number of substances identified and quantified before hemp treatment in samples is shown in Table 6 (identification) and Table 7 (quantification). A general analysis of all these results showed that industrial effluents contained both mineral and organic contamination and they are not constant in either quality or quantity. The number of contaminants (metals + other minerals + organics) were 45, 53 and 49 for W1, W2 and W3, respectively (Table 6). Of the 170 substances monitored, 40 were always found in wastewaters: 30 inorganics (16 metals and 14 other minerals) and 10 organics (3 VOCs, 4 APs, 1 CP and 2 PAHs). The quantities of contaminants in samples is important (Table 7). For instance, the values for W1 are 413 mg of metals, 5238 mg of other minerals, 232 µg of COVs, 79 µg of APs, 3.98 µg of CPs and 1.48 µg of PAHs for 1 L. The chemical composition in wastewaters can be ranked as follows: W2 > W3 > W1 for the number of substances, W3 > W1 > W2 for the quantities of metals, CPs and PAHs, W2 > W1 > W3 for the quantities of other minerals, and W2 > W3 > W1 for the quantities of COVs and APs.

Table 2 shows the analytical results obtained for water parameters measured, confirming the presence of a mineral and organic polycontamination in samples with a high degree of qualitative and quantitative variability. The wastewaters were slightly acidic (mean pH of 4.6 ± 0.3 at 20°C). They did not present significant turbidity (low levels of SS). On the other hand, they showed high conductivity (mean value of 9150 ± 2257 µS/cm at 20°C) and relatively high levels of organic pollution with a mean COD of 653 ± 176 mg/L and TOC of 84.7 ± 12.3 mg/L. High levels can also be seen in nitrates (205 ± 23 mg/L) and AOX (3550 ± 1502 µgCl/L). The cyanides (total and easily released), nitrites, free chlorine and hydrocarbon index were lower than the quantification limit (Table 2).

The results reported in Table 3 confirm the high salinity of wastewaters with high levels of sulphates (mean value of 3413 ± 732 mg/L), chlorides (1043 ± 129 mg/L), sodium (385 ± 53 mg/L), and calcium (318 ± 60 mg/L). Sixteen metals were found at quantifiable levels (Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn, Li, Sn, Sr, Ti and V). The concentration of other metals (Ag, As, Ba, CrVI, Sb, Hg, Pd, Pt, Te, Tl, W) remained below the limit of quantification. High levels can be seen in Fe (mean value of 337 ± 131 mg/L), Mn (27.5 ± 9.8 mg/L), Zn (19.8 ± 10.8 mg/L), Cu (8.64 ± 1.84 mg/L), Co (5.97 ± 3.53 mg/L), Ni (4.66 ± 0.80 mg/L), and Al (2.68 ± 2.02 mg/L). Fourteen other minerals (phosphorus, boron, magnesium, sodium, calcium, potassium, sulfur, silicon, fluorides, chlorides, bromide, sulphates, ammonium and nitrates) were systematically found in samples. Thirty-one organic substances were identified and quantified including 9 VOCs, 10 APs, 7 CPs and 5 PAHs (Table 4). However, only ten substances (chloroform, dichloromethane, nonylphenol, nonylphenol monoethoxylate, octylphenol monoethoxylate, 3-methylphenol, 2,4,6-trichlorophenol, 1,2-dichlorobenzene, phenanthrene and naphthalene) were systematically found in the three samples. High levels can be seen in chloroform (mean value of 233 ± 10 µg/L), nonylphenol (221.6 ± 138 µg/L), 1,2-dichlorobenzene (81.6 ± 28.8 µg/L), and tetrachloroethylene (9 ± 14.7 µg/L). Wastewaters did not contain any choroanilines, polychlorobiphenyls and organo-tin (values lower than the quantification limit).

Table 6. Recap of the total number of substances identified before and after hemp treatment in wastewaters noted W1, W2 and W3 (VOCs: volatile organic compounds; APs: alkylphenols; CPs: chlorophenols; PAHs: polycyclic aromatic compounds)

Wastewater	Metals	VOCs	APs	CPs	PAHs	Other inorganic contaminants[1]	Total
W 1	13	7	6	3	3	13	45
W1 treated by HEMP	11	6	4	2	0	13	36
W1 treated by HEMPBA	4	6	6	3	0	11	32
W1 treated by HEMPM	9	4	4	2	0	13	32
W1 treated by HEMPCD	8	0	1	2	0	13	24
W 2	16	7	8	6	3	13	53
W2 treated by HEMP	13	6	7	5	3	13	47
W2 treated by HEMPBA	5	7	8	6	3	13	42
W2 treated by HEMPM	12	6	7	6	2	13	46
W2 treated by HEMPCD	8	3	2	1	0	13	27
W 3	16	4	6	6	4	13	49
W3 treated by HEMP	11	3	3	5	4	13	40
W3 treated by HEMPBA	6	4	5	5	3	13	36
W3 treated by HEMPM	12	3	3	5	2	13	38
W3 treated by HEMPCD	9	1	1	2	0	13	26

[1]phosphorus, boron, magnesium, sodium, calcium, potassium, sulfide, silicon, fluorides, chlorides, bromide, sulphates, ammonium, nitrates

Table 7. Recap of the quantities of contaminants before and after hemp treatment in wastewaters noted W1, W2 and W3 (metals and other contaminants in mg/L; VOCs, APs, CPs and PAHs in µg/L)

Wastewater	Metals	VOCs	APs	CPs	PAHs	Other inorganic contaminants[1]	Total
W 1	13	7	6	3	3	13	45
W1 treated by HEMP	11	6	4	2	0	13	36
W1 treated by HEMPBA	4	6	6	3	0	11	32
W1 treated by HEMPM	9	4	4	2	0	13	32
W1 treated by HEMPCD	8	0	1	2	0	13	24
W 2	16	7	8	6	3	13	53
W2 treated by HEMP	13	6	7	5	3	13	47
W2 treated by HEMPBA	5	7	8	6	3	13	42
W2 treated by HEMPM	12	6	7	6	2	13	46
W2 treated by HEMPCD	8	3	2	1	0	13	27
W 3	16	4	6	6	4	13	49
W3 treated by HEMP	11	3	3	5	4	13	40
W3 treated by HEMPBA	6	4	5	5	3	13	36
W3 treated by HEMPM	12	3	3	5	2	13	38
W3 treated by HEMPCD	9	1	1	2	0	13	26

[1]phosphorus, boron, magnesium, sodium, calcium, potassium, sulfide, silicon, fluorides, chlorides, bromide, sulphates, ammonium, nitrates

3.2. Biological characterization of the wastewaters

Environmental legislation in Europe highlights the complementarity of combined chemical and biological monitoring approaches [1]. In France, the French Water Authority requires certain companies to carry out a biological test to assess the ecotoxicity of their treated wastewaters before discharging it into the environment, and this trend is becoming widespread. However, while contaminant mixtures present in water in general are relatively easy to characterize chemically, assessing their impact on the environment is usually difficult and has rarely been reported. In addition, the toxicity of surface treatment waste remains poorly defined [31]. In this work, the toxicity of the three wastewaters before hemp treatment was studied using two bio-indicators, *Daphnia magna* and *Lactuca sativa*.

The EC50 values for D. magna and germination rates for *L. sativa* given in Table 5 indicate high toxicity. According to a French guide on the use of bioassays for the quality assessment of samples, the effluents were classified toxic if EC50 < 50% and very toxic if EC50 < 10%. The EC50 are very low for Daphnis indicating deleterious effects on this bio-indicator. The results also confirm that contaminants present in wastewater inhibited the germination of planted seeds (Table 5). An important decrease of the germination rate is observed (average germination rate value of 15.5% ± 4.8; 95% ± 0.5% for the controls). Metals, other minerals, organics, and other unidentified substances such as commercial organic preparations used by industrial (data are not available) could be responsible for the observed toxicity for the two bio-indicators.

To resume the analytical and ecotoxicological data, our survey demonstrated the contaminant load in the three wastewaters studied, taken on three consecutive weeks, varied over time both quantitatively and qualitatively, indicating the great variability of the pollution present in the different samples. From a chemical point of view, the chemical composition in wastewaters can be ranked as follows: W2 > W3 > W1 for the number of substances, W3 > W1 > W2 for the quantities of metals, W1 > W2 > W3 for the total of organic load expressed as the sum of TOC and COD, and W2 > W3 > W1 for the total of organic substances expressed as the sum of quantities. For the two bioassays, the sample toxicity range (decreasing order) was W1 > W3 > W2 for D. magna and W2 > W3 > W1 for *L. sativa*.

3.3. Effect of hemp treatment on water parameters

In Table 8, the values of water parameters of samples and the same samples treated with hemp are shown. By comparing all the results obtained, HEMPCD is more efficient than HEMP, HEMPBA and HEMPM in removing contamination. HEMPCD decreases COD, TOC (Figure 1) and AOX but has little effect on nitrates (Table 8). The average values for COD are 653 mg/L ± 176 for wastewaters, 575 mg/L ± 201 for HEMP (corresponding to an abatement of 12%), 595 mg/L ± 198 for HEMPBA (9% abatement), 359 mg/L ± 174 for HEMPM (45% abatement) and 113 mg/L ± 29 for HEMPCD (83% abatement). These results clearly indicate the important role of cyclodextrin molecules to decrease organic load. This is also confirmed by the abatement values for TOC: 12%, 7%, 26 and 53% for HEMP, HEMPBA, HEMPM and HEMPCD, respectively. The average AOX value also decreases significantly after HEMPCD treatment (78% abatement). The three modified hemp materials, in the order HEMPM ~ HEMPCD < HEMPBA, decreased ammonium concentration, suggesting strong chemical interactions between carboxylate groups and ammonium groups, in agreement with literature data [39-41].

Table 8. Average values (standard deviation) for water parameters of three wastewaters before and after hemp treatment (*p*H at 20°C; conductivity in µS/cm at 20°C; concentrations expressed in mg/L; SS suspended solids; COD chemical oxygen demand; TOC total organic carbon; AOX adsorbable halogenated organic compounds)

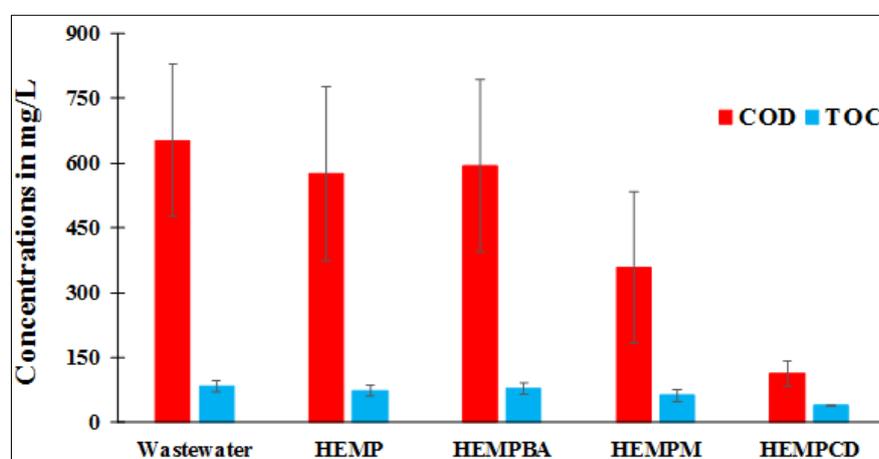| Parameter	Wastewater before treatment	Wastewater treated by HEMP	Wastewater treated by HEMPBA	Wastewater treated by HEMPM	Wastewater treated by HEMPCD
pH	4.7 (0.4)	4.8 (0.3)	4.9 (0.3)	5.1 (0.4)	5.3 (0.2)
conductivity	9150 (2257)	5750 (1689)	5083 (1355)	5150 (1676)	5333 (1527)
SS	22 (8)	16 (5)	17 (6)	15 (5)	15 (5)
COD	653 (176)	575 (201)	595 (198)	359 (174)	113 (29)
TOC	84.7 (12.3)	74.5 (12.6)	79 (12.8)	62.9 (13.7)	39.4 (1.2)
nitrates	205 (23)	180 (20)	205 (23)	193 (15)	197 (23)
ammonium	1.8 (0.8)	1.5 (0.5)	0.45 (0.26)	0.65 (0.27)	0.61 (0.22)
AOX	3550 (1502)	2450 (1076)	2333 (802)	1633 (592)	763 (131)

Figure 1. Concentrations (in mg/L) of chemical oxygen demand (COD) and total organic carbon (TOC) parameters for the three wastewaters before (raw wastewater) and after hemp treatment (HEMP, HEMPBA, HEMPM and HEMPCD)

3.4. Effect of hemp treatment on inorganic contaminant removal

The data presented in Table 9 show a significant elimination of metal contamination for each wastewater treated by hemp. However, the proposed treatment, using the conditions described in the material and method section, is not able to remove all substances present as reported in Table 7. Indeed, the main objective of this study was not to obtain optimal performance (which can be obtained by increasing the dose of material for example, as already published) [27,28] but to highlight the role of the material structure in its performance.

The four felts are efficient in reducing the metal load in effluents (Table 9, Figure 2), whatever the metal considered, but as expected, the abatements are very high for modified materials (Figure 2), pointing out the important role of carboxylate groups in chemisorption mechanism. These groups are responsible for metal cations binding through electrostatic interactions and ion-exchange [39-41], and their presence in HEMPBA, HEMPM and HEMPCD (respectively 1.41, 1.08 and 1.18 meq COOH groups per gram, against 0.19 meq/g for raw hemp) positively influenced their performance. Adsorption mechanism have already been discussed using data from scanning electron microscopy and energy-dispersive X-ray spectroscopy studies in our previous work [27,28]. HEMP is nevertheless effective in reducing the metallic load in samples, with metal-dependent performance. Good abatements have been obtained for Co, Fe, Ni, Mn, Zn and especially Cu (Table 9, Figure 2), in agreement with our previous works [26,29].

Comparing all the results obtained, the highest levels of metal removal are achieved with HEMPBA (Tables 7 and 9, Figure 2), whatever the wastewater treated, and this treatment effectively lowers the main metals, namely Al, Co, Cu, Fe, Mn, Ni and Zn, present in industrial wastewater (Table 9). For instance, for the three effluents, the average values for Zn are 19.8 mg/L ± 10.8 for wastewaters, 9.2 mg/L ± 6.9 after treatment with HEMP (53% abatement), 3.63 mg/L ± 0.46 for HEMPM (81% abatement), 1.36 mg/L ± 1.1 for HEMPCD (93% abatement), and 0.213 mg/L ± 0.255 for HEMPBA (98.7% abatement). The average values of Al, Ni and Cu concentrations also decrease significantly after HEMPBA treatment. The levels for Cd, Cr, Cu, Mo, Ni, Pb, Li, Ti, Sn, Sr and V are below the limit of quantification (Table 9). Compared to HEMP, HEMPM and HEMPCD are more efficient in removing metals, reconfirming the role of carboxylate groups in the adsorption mechanism. However, the performance obtained for these two materials was lower than that obtained with material HEMPBA (Tables 7 and 9). So, the metal cations uptake by the materials can be correlated with their respective ion-exchange capacity (Table 1). In particular, as observed in Scheme 2, in the case of HEMPM and HEMPCD, two of the four carboxylic groups of BTCA are transformed into ester groups to provide a covalent bond with cellulose of hemp on the one hand, and with maltodextrin or cyclodextrin on the other hand, or a cross-linking between two maltodextrins or two cyclodextrins. Interestingly, in case of HEMPBA, probably cross-linking between two cellulose chains exposed on the surface of hemp occurs, but it can be supposed that BTCA can also be grafted on cellulose through only one ester linkage, resulting in three residual free carboxylic functions per BTCA instead of two. As a consequence, as confirmed by the titration assays, HEMPBA samples present more carboxylic groups with a better accessibility than those present on HEMPM and HEMPCD samples.

Notable differences are observed for Mn (Table 9, Figure 2). The average values for this metal are 25.7 mg/L ± 9.8 for wastewaters, 25 mg/L ± 8.3 for HEMP, 3.44 mg/L ± 1.2 for HEMPCD, 3.81 mg/L ± 0.83 for HEMPM and 2.6 mg/L ± 0.7 for HEMPBA. These results clearly indicate a greater affinity for the carboxylate groups present in the modified felts (HEMPBA, HEMPM and HEMPCD) compared to raw felt (HEMP), confirming our previous results on Mn [27-29]. This higher removal corresponds to the preference of the carboxylate groups for this metal in accordance with HSAB theory for Pearson [43-45] and the classification proposed by Nieboer and Richardson [46]. In this theoretical concept, carboxylate groups are considered as hard base and then prefer hard acids such as Mn ions.

Modified materials were more efficient than HEMP to remove other inorganic contaminants. They decreased phosphorus, boron, calcium, potassium and sulfur concentrations (Tables 7 and 9), but had, as expected, no effect on fluorides, chlorides, bromide and sulphates, due to their anionic nature, which adversely affects interactions with carboxylate groups. Another observation must be noted (Table 9): an increase in the concentration of the sodium cations after hemp treatment, coupled with a decrease in the concentration of the metal ions, was systematically observed, indicating the replacement of the sodium cations by ion exchange. This has been demonstrated using energy-dispersive X-ray spectroscopy data, as recently published [27].

Table 9. Average values (standard deviation) for inorganic contaminants of three wastewaters before and after hemp treatment (concentrations expressed in mg/L)

Contaminant	Wastewater before treatment	Wastewater treated by HEMP	Wastewater treated by HEMPBA	Wastewater treated by HEMPM	Wastewater treated by HEMPCD
aluminum	2.68 (2.02)	1.8 (1.4)	0.307 (0.205)	0.82 (0.44)	0.55 (0.3)
cadmium	0.116 (0.031)	<0.002	<0.002	0.028 (0.045)	<0.002
cobalt	5.97 (3.53)	3.2 (1.8)	0.607 (0.251)	1.4 (0.67)	1.15 (0.566)
chromium	0.73 (0.55)	0.26 (0.15)	<0.005	0.16 (0.05)	0.15 (0.087)
copper	8.64 (1.84)	2.1 (0.3)	<0.005	0.89 (0.618)	0.53 (0.335)
iron	337 (131)	80.7 (23.1)	35.8 (13.7)	58.1 (17.2)	50.3 (12.9)
manganese	25.7 (9.8)	25 (8.3)	2.6 (0.7)	3.81 (0.83)	3.44 (1.2)

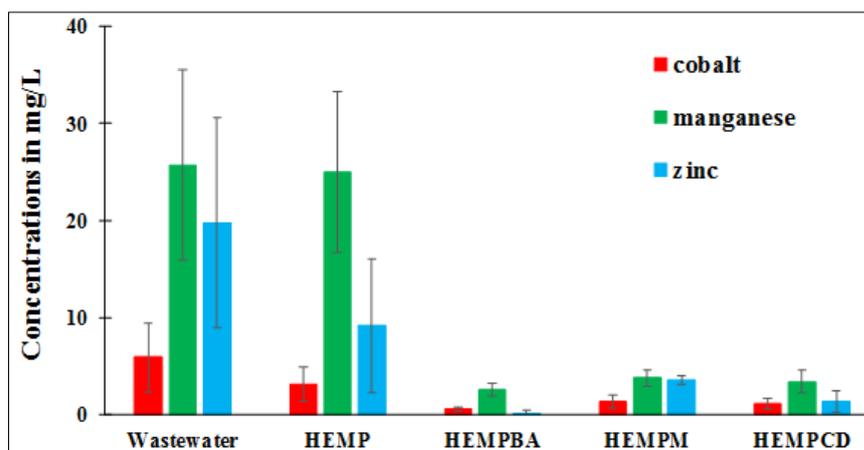|					
molybdenum	0.27 (0.11)	0.13 (0.05)	<0.01	0.057 (0.045)	<0.01
nickel	4.66 (0.8)	1.12 (0.22)	<0.01	0.057 (0.045)	<0.01
lead	0.046 (0.039)	<0.002	<0.002	<0.002	<0.002
zinc	19.8 (10.8)	9.2 (6.9)	0.213 (0.255)	3.63 (0.46)	1.36 (1.1)
lithium	0.061 (0.037)	0.03 (0.017)	<0.02	<0.02	<0.02
tin	0.05 (0.028)	0.017 (0.015)	<0.005	0.007 (0.003)	<0.005
strontium	0.505 (0.163)	0.23 (0.07)	<0.02	0.13 (0.05)	0.05 (0.05)
titane	0.123 (0.102)	0.081 (0.069)	0.02 (0.02)	0.07 (0.05)	0.03 (0.03)
vanadium	0.038 (0.02)	0.011 (0.001)	<0.01	<0.01	<0.01
magnesium	107 (39)	99.3 (36.4)	70.1 (26.8)	83.8 (27.9)	84.4 (35.7)
phosphorus	1.167 (0.076)	0.84 (0.056)	0.647 (0.119)	0.523 (0.046)	0.386 (0.021)
boron	42.6 (6.7)	35 (5.6)	20.4 (10.5)	29.4 (5)	28.7 (12.1)
sodium	385 (53)	340 (46)	500 (50)	577 (93)	575 (139)
calcium	318 (60)	298 (55)	247 (55)	257 (93)	242 (52)
potassium	33.6 (9.2)	32.1 (9.5)	24.1 (7.8)	29.8 (8.4)	29.7 (9.6)
sulfur	27.3 (7.8)	23.2 (5.5)	17.4 (4)	18.1 (6.3)	17.5 (6.1)
silicon	17.5 (2.5)	16.4 (2.1)	11.8 (1.3)	13.9 (1.9)	14.1 (1.2)
fluorides	19.5 (3.6)	13.5 (4.4)	19 (2.7)	17.5 (2.8)	17 (3.8)
chlorides	1043 (129)	823 (155)	980 (101)	942 (101)	900 (87)
bromide	57.7 (21.1)	40.9 (19.4)	57.7 (21.1)	54.7 (21.6)	52.3 (18.6)
sulphates	3413 (732)	2767 (833)	3380 (755)	3183 (711)	3017 (729)

Figure 2. Concentrations (in mg/L) of cobalt, manganese and zinc for the three wastewaters before (raw wastewater) and after hemp treatment (HEMP, HEMPBA, HEMPM and HEMPCD)

3.5. Effect of hemp treatment on organic contaminant removal

The data presented in Table 10 and Figure 3 show a significant elimination of organic substances present in wastewaters treated by HEMPCD, with an important decrease of chloroform, nonylphenol, 1,2-dichlorobenzene and toluene. For instance, the average values for nonylphenol are 222 µg/L ± 138 for wastewaters, 163 µg/L ± 109 after HEMP treatment (26% abatement), 175 µg/L ± 115 for HEMPBA (14% abatement), 60 µg/L ± 28 for HEMPM (72% abatement) and 4.7 µg/L ± 0.8 for HEMPCD (97.8% abatement). The levels of others contaminants are in the vicinity of or even below the limit of quantification after both HEMPCD and also HEMPM treatment. The total amount of organics (VOCs+APs+CPs+PAHs) decreases from 316 µg for W1 to 185 µg, 211 µg, 91 µg and 15.9 µg for HEMP, HEMPBA, HEMPM and HEMCD treatments, respectively, showing that HEMPM and especially HEMPCD are able to remove the organic substances present in W1. Similar results were

obtained for W2 and W3. The analysis of the results presented in Tables 7 and 10 also confirms that HEMP and especially HEMPBA are not very effective in reducing the organic load in wastewater even if some concentrations have decreased. For HEMPBA, it seems that its anionic and more hydrophilic nature disadvantages interactions with organics, whereas for HEMPM, the presence of the maltodextrin cross-linked polymer makes it possible to eliminate them. However, HEMPM was less effective than HEMPCD (Tables 7 and 10), whatever the wastewater treated, pointing out the important role of the cyclodextrin cavity in the adsorption mechanism. Indeed, considering both linear and cyclic dextrins, the chemical composition of the corresponding coatings on hemps is perfectly identical and the results obtained show that the organic pollutants specifically interact with the two cross-linked dextrins immobilized on the hemp fibers. However, the increased performances observed for HEMPCD compared to HEMPM clearly shows the benefit of the cavity of HPβCD (Figure 3), which are responsible for the removing of contaminants by inclusion complexation [47]. It should be mentioned that among the abundant literature on cyclodextrin-based sorbents applied to wastewater de-contamination and also to drug delivery systems, almost no studies report the use of a maltodextrin-based material as a control to highlight the involvement of host-guest phenomena in interactions between materials and pollutants or drugs.

Table 10. Average values (standard deviation) for organic contaminants of three wastewaters before and after hemp treatment (concentrations expressed in µg/L)

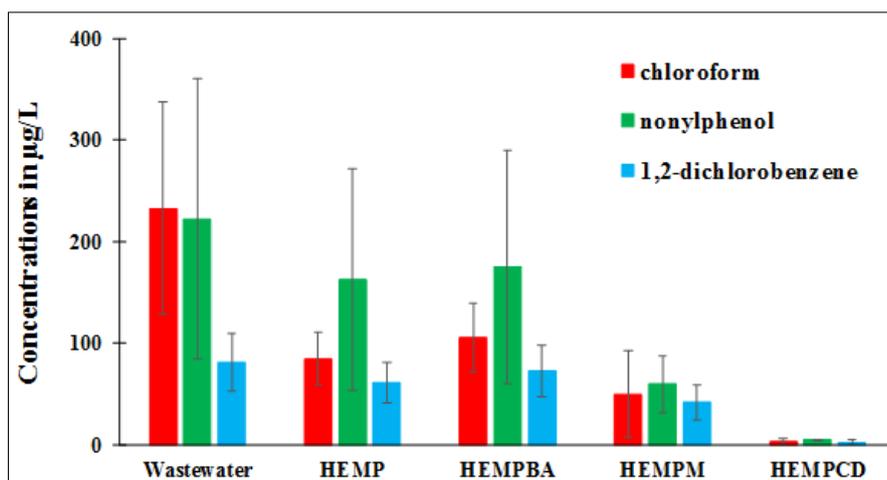| Contaminant	Wastewater before treatment	Wastewater treated by HEMP	Wastewater treated by HEMPBA	Wastewater treated by HEMPM	Wastewater treated by HEMPCD
chloroform	233 (104)	85 (26)	106 (34)	50 (43)	3.6 (2.8)
1,2-dichloroethane	3.22 (3.14)	0.95 (0.39)	2.83 (2.77)	1.24 (0.88)	<0.5
dichloromethane	6.3 (1.15)	0.89 (0.49)	1.84 (1.29)	2.32 (2.42)	1.67 (2.89)
tetrachloroethylene	9 (14.7)	7 (11.2)	7.33 (11.8)	1.7 (2.08)	<0.5
trichloroethylene	1.07 (0.5)	<0.5	<0.5	<0.5	<0.5
nonylphenol	222 (138)	163 (109)	175 (115)	60 (28)	4.7 (0.8)
4-tert-octylphenol	1.67 (2.02)	<0.5	1.52 (1.76)	0.7 (0.35)	<0.5
4-tert-butylphenol	1.77 (2.89)	1.06 (1.67)	1.73 (2.83)	0.73 (1.1)	<0.5
nonylphenol monoethoxylate	0.29 (0.16)	0.13 (0.07)	0.26 (0.15)	0.12 (0.07)	<0.1
nonylphenol diethoxylate	1.87 (1.64)	1.28 (0.85)	0.85 (1.77)	1.58 (0.53)	<0.1
2-methylphenol	0.06 (0.01)	0.05 (0)	<0.05	<0.05	<0.05
3-methylphenol	0.12 (0.07)	0.07 (0.03)	0.09 (0.07)	0.07 (0.03)	<0.05
4-methylphenol	0.06 (0.01)	0.05 (0)	0.06 (0.01)	<0.05	<0.05
2-chlorophenol	0.23 (0.24)	0.12 (0.12)	0.23 (0.24)	0.12 (0.12)	<0.05
4-chlorophenol	0.37 (0.55)	0.36 (0.54)	0.37 (0.55)	0.25 (0.35)	<0.05
2,4-dichlorophenol	0.72 (0.6)	0.46 (0.48)	0.68 (0.55)	0.36 (0.42)	<0.05
2,3-dichlorophenol	0.06 (0.02)	0.05 (0)	0.06 (0.02)	<0.05	<0.05
3,4-chlorophenol	0.08 (0.06)	0.07 (0.03)	0.08 (0.06)	0.07 (0.03)	<0.05
2,4,6-trichlorophenol	2.75 (0.8)	1.98 (0.58)	2.4 (0.52)	1.05 (0.71)	<0.25
1,2-dichlorobenzene	81.6 (28.8)	61.4 (19.9)	72.9 (25.7)	41.9 (17.3)	2.37 (2.51)
4-chloro-3-methylphenol	0.12 (0.144)	<0.05	0.14 (0.16)	0.11 (0.1)	<0.05
toluene	14.7 (12.3)	8 (7)	12.7 (10.7)	5 (5.3)	<1
anthracene	0.12 (0.1)	0.07 (0.11)	0.01 (0)	0.01 (0)	<0.01
phenanthrene	0.19 (0.02)	0.08 (0.06)	0.09 (0.07)	0.01 (0)	<0.01
naphthalene	1.05 (0.52)	0.49 (0.56)	0.49 (0.5)	0.29 (0.3)	<0.01
fluoranthene	0.133 (0.005)	0.08 (0.06)	0.09 (0.07)	<0.01	<0.01
pyrene	0.013 (0.005)	<0.01	<0.01	<0.01	<0.01
ethylbenzene	0.49 (0.83)	0.23 (0.38)	0.37 (0.63)	0.41 (0.69)	0.29 (0.48)
isopropylbenzene	0.87 (0.32)	0.8 (0.26)	0.8 (0.26)	0.55 (0.09)	0.37 (0.22)

Figure 3. Concentrations (in µg/L) of chloroform, nonylphenol and 1,2-dichlorobenzene for the three wastewaters before (raw wastewater) and after hemp treatment (HEMP, HEMPBA, HEMPM and HEMPCD)

3.6. Effect of hemp treatment on water toxicity

From a chemical point of view, treating the wastewaters has helped not only to reduce the concentration of contaminants but also to completely eliminated part of them (concentration under QL). The total number of substances identified and quantified before and after hemp treatment in samples is shown in Tables 6 and 7. Before treatment, the number of contaminants were 45, 53 and 49 for W1, W2 and W3, respectively. After hemp treatment, the number of substances decreased (Table 6), whatever the wastewater and the material used. Nevertheless, notable differences were observed. HEMPBA was particularly effective in complexing metals (e.g. for W1, the number of metals were 14 and 5 before and after treatment, respectively), while the best performance for organic substances was obtained with HEMPCD (Tables 6 and 7). To confirm this positive impact and to evaluate the environmental benefits of the chemical treatment on water toxicity, bioassays were performed. To this end, measurements of inhibition of *D. magna* mobility and of germination rate of *L. sativa* seeds were also carried out on wastewater after hemp treatment, and compared with those obtained before treatment. The results given in Table 11 compare the potential toxicity of wastewaters on bio-indicator *D. magna* with that of the same effluents after adsorption on the proposed four materials. After hemp treatment, the impact on *D. magna* was reduced, as indicated by higher EC values, whatever the material used. For instance, daphnid EC50 values were 0.7% for W1 and 46.3%, 79.3%, 84.3% and > 90% for the same wastewater treated by HEMP, HEMPBA, HEMPM and HEMPCD, respectively. Decreasing concentrations of contaminants in wastewater W1 led to a significant reduction of their impact on daphnid immobility. For the three wastewaters, the treatment by HEMPCD gave better results since exposure to the wastewaters for 24h did not cause immobilization (EC50 > 90%, Table 11).

Table 11. Toxicity values expressed by EC50 in percentage of wastewater for *Daphnia magna* for three samples before and after hemp treatment (n = 1)

Wastewater	Wastewater before treatment	Wastewater treated by HEMP	Wastewater treated by HEMPBA	Wastewater treated by HEMPM	Wastewater treated by HEMPCD
W1	0.7	46.3	79.3	84.3	> 90
W2	3.1	55.8	77.3	82.3	> 90
W3	2.7	54.3	75.9	81	> 90

A bioassay based on the germination rate of *L. sativa* seeds was also performed on samples after hemp treatment. Figure 4 compares the germination success of seeds soaked in wastewaters and the same effluents treated by hemp. The average germination rate values (n = 3) were: 95% ± 5 for the controls, 15.5% ± 4.8 for wastewaters, 62.9% ± 5.7 after HEMP treatment, 89.5% ± 2.2 after HEMPBA treatment, 83.4% ± 1.7 after HEMPM treatment, and 94.7% ± 1.4 after HEMPCD treatment. All the materials including HEMP exhibit good improvement of germination rates. After HEMPBA and HEMPCD treatment, the impact on lettuce germination is considerably reduced, suggesting contaminant removal by these two materials obviously decreases the water toxicity.

The two biological tests used in this work made it possible to show the interest of a better chemical efficiency from the point of view of the reduction of contaminants on the toxicity of water. In addition, they have demonstrated that the benefits of this efficiency can lead to an environmental gain, i.e. less toxic industrial effluent when released into the environment.
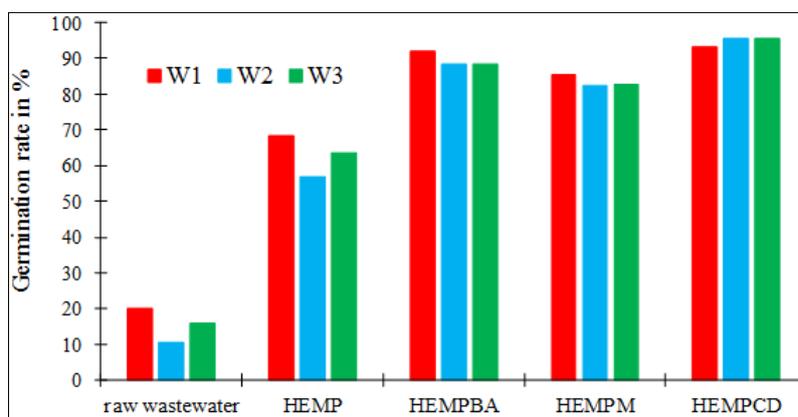

Figure 4. Variations in Lactuca sativa seed germination
(n = 3) for the three wastewaters before (raw wastewater)
and after hemp treatment (HEMP, HEMPBA, HEMPM and HEMPCD)

4. Conclusions

In this study, added value was added to hemp-based materials through environmentally friendly chemical modification. This work demonstrated that adsorption on these materials in the form of felt could be a practical and effective step to significantly reduce metals and organic substances in polycontaminated industrial wastewaters containing high contaminant loads and, consequently, their toxicity. Of the four materials proposed, hemp simply modified with BTCA had the best absolute performance for metal decontamination. However, only felt coated with hydroxypropyl-β-cyclodextrin-1,2,3,4-butanetetracarboxylic cross-linked polymer was able to effectively remove metals and organics at the same time, highlighting the important role of both the carboxylate groups and cyclodextrin molecules grafted on felt. Bioassays, consisting of measurements of mobility inhibition *of Daphnia magna* and of the germination rate of *Lactuca sativa* seeds carried out on wastewaters before and after hemp treatment, confirmed the effectiveness of hemp treatment in dramatically reducing effluent toxicity, especially when the felt coated with hydroxypropyl-β-cyclodextrin-1,2,3,4-butanetetra-carboxylic cross-linked polymer was used. The obtained results in terms of chemical abatement and toxicity mitigation have demonstrated that adsorption onto a nonconventional material could be an interesting treatment step for the detoxification of industrial wastewater. Here, the modified felts were used in batch processes but in future applications they could be used as a bag filter. Also more experiments will be carried out using other real effluents.

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