

CONCENTRATION OF CADMIUM(II) TRACE AMOUNTS FROM LARGE VOLUMES OF AQUEOUS SAMPLES ON CHEMICALLY MODIFIED HEMP FIBERS

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This study reveals the results of experiments designated to emphasize the practical usefulness of sulphhydryl hemp fibers. The concentration of trace amounts of Cd (II) from large volumes of aqueous samples on sulphhydryl hemp fibers was carried out under batch conditions. It was found that by using this material the concentration of cadmium in wastewaters might be reduced below allowable discharge limits. The recovered cadmium was greater than 95% and cadmium concentration factors over 30 were realized. More than 78% of cadmium(II) was recovered with 2M HNO₃. By calcining sulphhydryl hemp fibers at 800°C and dissolution of the obtained residue with HCl 1: 1, the percentage of cadmium recovery exceeded 95%. The results of this study suggest that sulphhydryl hemp fibers may be a promising sorbent provided for environmental technologies in the future.

Key words: cadmium, hemp fibers, sulphhydryl groups, concentration

Population expansion and increased industrialization have contributed to the release of increased heavy metals content in the environment. The ubiquitous nature of heavy metals, their toxicity even in traces, their tendency for bioaccumulation in food chain, their non-biodegradability, their ability to undergo transformations, the economic impact and the stricter environmental regulations related to heavy metals discharges have prompted the development of new processes for the removal of heavy metals from aqueous effluents.

Various methods for the removal of heavy metals from aqueous media include chemical precipitation, ion exchange, electro-dialysis, reverse osmosis, membrane filtration and sorption. Sorption is one of the recognized efficient processes of heavy metals removal from aqueous solutions. In spite of the usefulness and effectiveness of alumina, silica, iron oxide and activated carbon as sorbents of heavy metals, their prohibitive costs have restricted their widespread use. Sorption processes using natural or agricultural and industrial waste products are becoming the new alternative for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and land investment. Among the

agricultural and industrial wastes peat, wood, tree bark, sawdust, granular slag are numbered[1-5, 7,12,19].

Hemp is a commonly available and inexpensive cellulosic material showing remarkable sorption properties for heavy metals, both in natural and modified form. The high mechanical strength and porosity, hydrophilic character, faster sorption, tolerance to biological structures and easiness in functionalisations make the hemp fibers superior to the other unconventional sorbents[6,9,10,11]. Thus, the batch sorption of four toxic and polluting metal ions, viz. Cr(III), Cu(II), Ag(I) and Cd(II) on natural hemp fibers has been studied[8,13]. The monolayer sorption capacity was 4.0006, 9.0735, 1.2253 and 2.5909 mg/g hemp for chromium(III), copper(II), silver(I) and cadmium(II) ions, respectively at 18°C. The following relative affinity of cation sorption on natural hemp: Cu(II)>Cr(III)>Cd(II)>Ag(I) has been established. In order to improve the sorption performances of this material, the hemp fibers have been physically and chemically modified. Some unconventional sorbents obtained by loading of natural hemp and hypochlorite bleached hemp fibers with α -benzoinoxime can be efficiently used as selective material for Cu(II) ions [14,15]. Although both materials possess important sorptive properties, there is significant differences between Cu(II) sorption capacity of hemp- α -benzoinoxime (13.8072mg/g) and bleached hemp fibers impregnated with the same chelating agent(8.0378mg/g). The decreased sorption affinity of the bleached hemp loaded with α -benzoinoxime may be considered as an effect of the hypochloride oxidation on hemp fibers. Impregnating alizarine S on natural hemp resulted in a sorbent showing higher affinity towards Cr(III) ions compared to natural cellulosic fibers[16]

The sorption and kinetic properties of a material prepared by introducing sulphhydryl (-SH) functional groups into natural hemp fibers in batch retention of Ag(I), Cd(II) and Pb(II) ions have been reported[17]. This work reveals the results of some tests designated to emphasize the effectiveness of the sulphhydryl hemp fibers for the concentration, separation and determination of Cd(II) in traces.

MATERIAL AND METHOD

The sulphhydryl hemp fibers were prepared according to the procedure used in the synthesis of a chelating sorbent with sulphhydryl functional groups from natural cotton fibers and thioglycolic acid[17]. (Fig. 1) describes the method that was applied for chemical modification of natural hemp fibers with β -mercaptopropionic acid and acetic anhydride.

Different volumes of solution (200ml, 500ml and 1000ml) containing the same amount of Cd(II)(112 μ g) were added to 25 g of sulphhydryl hemp fibers. The samples were equilibrated and shaken for 24 hours at room temperature, after which the samples were filtered. Cd loaded sorbent obtained from one sorption experiment was transferred to Erlenmeyer flask and shaken with 25 mL of HNO₃ 2M. Into another three desorption experiments, Cd loaded sulphhydryl hemp fibers were calcinated at 800°C and the obtained residues were dissolved with 25 mL of HCl 1:1. The filtrate and the solutions previously obtained were analyzed using a Perkin-Elmer 3300 atomic absorption spectrophotometer for desorbed cadmium.

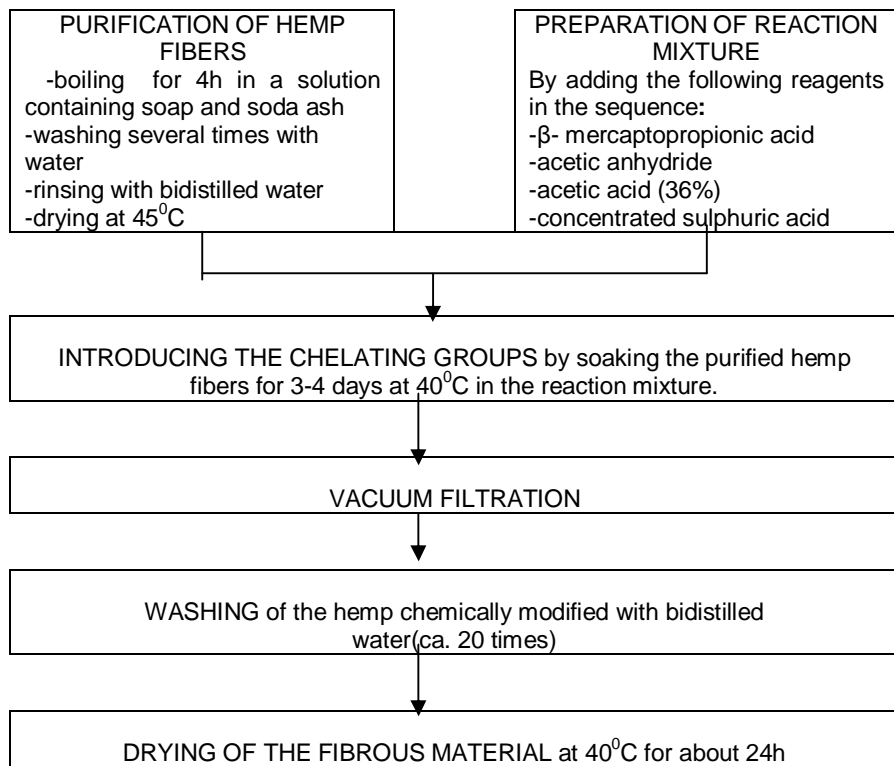


Figure 1 **Scheme of sulphydryl hemp fibers preparation**

RESULTS AND DISCUSSIONS

Although by introducing sulphydryl functional groups into natural hemp fibers a considerable change in the cellulosic fibrous material was made, their fundamental physical – chemical characteristics were unaffected (*fig. 2*)

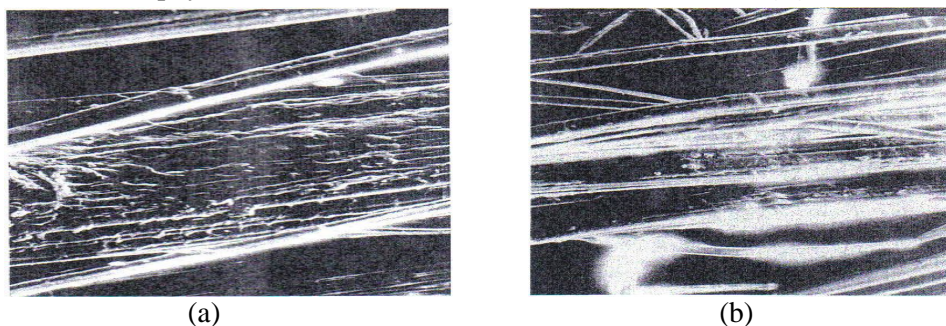


Figure 2 **Electron micrographs of: a) natural hemp fibers; b) natural hemp fibers functionalized with β-mercaptopropionic acid**

The results of a systematic study on the cadmium(II) ions sorption characteristics and kinetic properties of the sulphhydryl hemp fibers are recorded in (tab.1) [17].

Table 1

**Quantitative description of the sorption system hemp – SH – Cd(II)(pH =5.75;
working range of concentration:4.5 – 67.3μg/mL)**

Langmuir constants		Freundlich constants		Sorption rate constant (min ⁻¹)
q ₀ (mmol/g)	K _L	K _F	n	
0.125	7.547	2.37	7.76	1.632x10 ⁻²

In order to emphasize the practical usefulness of the chelating sorbent based on sulphhydryl hemp fibers, the concentration of trace amounts of cadmium (II) from large amounts of aqueous solutions have been carried out. The desorption studies were also performed to see the elution of cadmium from the point of view of its recycling/ safe disposal(with or without treatment). The results of these experiments are listed in (tab.2). It must be noticed that the values of the concentration factor in (tab.2) were calculated by means of following equation[18]:

$$\text{Concentration factor} = \frac{q_k \cdot V_{\text{sample}}}{q_{\text{sample}} \cdot V_k}$$

where: q_k and q_{sample} = the absolute amounts of Cd(II) in concentrate and sample, respectively; V_k= volume of concentrate; V_{sample} = volume of the sample.

It may be noticed that the batch experiments were conducted in replicates (n=4) and the data listed in (tab.2) represents the mean value. Furthermore, the following statistical parameters have been calculated [18]:

$$\bar{X} = \frac{x_1 + x_2 + \dots + x_n}{n} \quad \text{the arithmetic mean}$$

$$s^2 = \frac{\sum_{i=1}^n (\bar{X} - x_i)^2}{n - 1} \quad \text{the selection variance}$$

$$s = \sqrt{\frac{\sum_{i=1}^n (\bar{X} - x_i)^2}{n}} \quad \text{the mean square deviation}$$

$$s_x = \frac{s}{\sqrt{n}} \quad \text{the mean square deviation of the selection mean}$$

$$E\% = \frac{s_x \cdot 100}{\bar{X}} \quad \text{relative error}$$

$$\bar{X} \pm \frac{t \cdot s}{\sqrt{n}} \quad \text{the confidence interval(t is Student coefficient (95\%)=3.18)}$$

The obtained values for these statistical parameters are given in (tab.3).

Table 2.

Concentration of Cd(II) in traces by hemp – SH ($V_k = 25$ mL)

Experiment	V_{sample} , mL	Initial amount of Cd(II), μg	Cd(II) $\mu\text{g/mL}$	Cd(II) found, μg	Concentration factor	Remarks
1.	200	112	0.560	88.1	6.29	Elution with HNO_3 2M
2.	200	112	0.560	109.4	7.81	Calcining sulphhydryl hemp at 800°C and dissolution of the obtained residue with HCl 1: 1
3.	500	112	0.224	96.8	17.29	
4.	1000	112	0.112	87.7	30.27	

Table 3

Statistical analysis

Experiment	s^2	s	s_x	E%	Confidence interval
1.	0.0300	0.1732	0.0866	1.37	6.29 ± 0.2753
2.	0.0300	0.0550	0.0275	0.35	7.81 ± 0.0875
3.	0.6819	0.8257	0.4128	2.38	17.29 ± 2.6250
4.	0.5679	0.7535	0.3767	1.24	30.27 ± 1.1979

The data from (tab.2 and tab.3) show that by optimizing experimental factors and errors minimization, the use of sulphhydryl hemp fibers can lead to the decrease of the cadmium concentration from large volumes of wastewaters below allowable discharge limits. As can be seen from (tab. 2), the achieved values of cadmium concentration factors ranged between 6.29 and 30.27. The sorbed cadmium was subsequently eluted with nitric acid 2M, when a desorption of 78.66% was attained. However, an almost quantitative recovery of the sorbed cadmium(II) (97.67%) was possible by calcining Cd loaded sulphhydryl hemp fibers at 800°C and dissolution of the obtained residue with hydrochloric acid 1:1.

The results of this study suggest a sustainable and economical option for developing effluent treatment process for removal and recovery of cadmium.

CONCLUSIONS

It was found that by using sulphhydryl hemp fibers the concentration of cadmium in wastewaters might be reduced below allowable discharge limits. The recovered cadmium was greater than 95% and cadmium concentration factors over 30 were realized. More than 78% of cadmium(II) was recovered with 2M HNO_3 . By calcining sulphhydryl hemp fibers at 800°C and dissolution of the obtained residue with HCl 1: 1, the percentage of cadmium recovery exceeded 95%.

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