CROATICA CHEMICA ACTA
CCACAA **77** (4) 581–586 (2004)

ISSN-0011-1643
*CCA*-2962
*Original Scientific Paper*

# Sorption Studies of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ Ions on Sulphydryl Hemp Fibers

**Lavinia Tofan and Carmen Paduraru***

*»Gh. Asachi« Technical University, Department of Analytical Chemistry, D. Mangeron Street 71, 6600 Jassy, Romania*

RECEIVED APRIL 24, 2002; REVISED NOVEMBER 7, 2003; ACCEPTED DECEMBER 12, 2003

*Key words*
sorption
hemp
cations
retention
sulphydryl groups

Results of a systematic study on the $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions sorption characteristics and kinetic properties of an unconventional material produced by introducing sulphydryl functional groups into natural hemp fibers are presented and discussed. The equilibrium data are analyzed using the Langmuir and Freundlich isotherm models. The monolayer sorption capacity of modified hemp is 10.75, 14.05 and 23.00 mg $g^{-1}$ for silver, cadmium and lead ions, respectively, at 18 °C. The constant of sorption rates calculated by the Lagergren equation is $5.806\times10^{-2}$ $min^{-1}$ for $Ag^{I}$, $1.632\times10^{-2}$ $min^{-1}$ for $Cd^{II}$ and $4.078\times10^{-2}$ $min^{-1}$ for $Pb^{II}$ ions. The systems under study offer some new attractive possibilities of selective sorption of various pollutants from aqueous effluents.

## INTRODUCTION

The need to eliminate some major disadvantages of sorbents based on synthetic organic polymers as well as the general tendency to replace chemical products by natural ones were the incentives for this research, where some unconventional materials for wastewater treatment were studied. These materials, mainly of cellulosic origin, include tree bark, rice straw, sugarcane bagasse, bamboo pulp, sawdust, and cotton, flax and jute fibers.

Their remarkable fundamental properties (low cost, availability, high mechanical strength and porosity, hydrophilic character, fast sorption, tolerance to biological structure, easy functionalization, possibility of being used as grains of various size, fibers and filters) explain the increasing attention paid by different workers to these unconventional cellulosic substrates.[1–7]

In this context, we used hemp, another commonly available and inexpensive cellulosic material, both in natural and modified forms,[8–12] in static and dynamic systems for $Cu^{II}$, $Cr^{III}$, $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions sorption.

We used a chelating sorbent prepared by introducing sulphydryl (-SH) functional groups into natural hemp fibers. In order to obtain a cheap and effective method of removing metal ions detrimental to life quality, the sorption and kinetic properties of this material in batch retention of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ cations from their aqueous solutions were assessed.

## EXPERIMENTAL

### *Sorbent Synthesis*

The sulphydryl hemp fibers were prepared according to the procedure used in the synthesis of a chelating sorbent with sulphydryl functional groups from natural cotton fibers and thioglycolic acid.[13]

* Author to whom correspondence should be addressed. (E-mail: cpadur@email.ro)

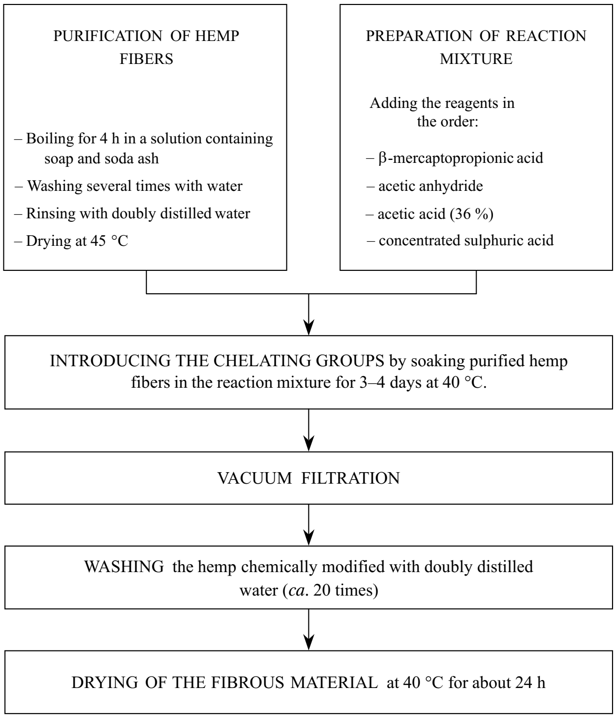


Figure 1. Scheme of chelating sorbent preparation.

Figure 1 describes the method that was used for chemical modification of natural hemp fibers with β-mercaptopropionic acid and acetic anhydride.

### *Reagents and Solutions*

Stock solutions of $10^{-2}$ mol dm$^{-3}$ were prepared by dissolution of $AgNO_3$, $Cd(CH_3COO)_2 \times 2H_2O$ and $Pb(NO_3)_2$ and were standardized gravimetrically. Working aqueous solutions of $Ag^I$, $Cd^{II}$ and $Pb^{II}$ were prepared by appropriate dilutions of stock solutions.

### *Sorption Properties*

The sorption properties of sulphydryl hemp fibers were studied in batch conditions of $Ag^I$, $Cd^{II}$ and $Pb^{II}$ cations retention. For this purpose, samples of about 0.5 g of sulphydryl hemp fibers were equilibrated for 24 h at 18 °C with 25 mL of each aqueous solution containing defined amounts of metal ions. The mixture was then filtrated and the solution was analyzed for the cation content. The amount of metal ions sorbed on sulphydryl hemp fibers was calculated from the difference between the initial and final concentrations of the solution.

All solutions were analyzed using a Perkin-Elmer 3300 atomic absorption spectrophotometer.

### *Kinetic Properties*

About 0.5 g of sulphydryl hemp fibers were magnetically stirred for 1 h with 200 mL of the diluted metal ion aqueous solutions. During the experiment, 0.5 mL of solution was taken periodically and in these samples, after requisite dilution, the cation concentration was determined by atomic absorption spectrometry. It is taken that the volume of, at most, 5 mL of sample withdrawn during each experiment has no major influence upon the entire volume of aqueous solution under study.

## RESULTS AND DISCUSSION

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

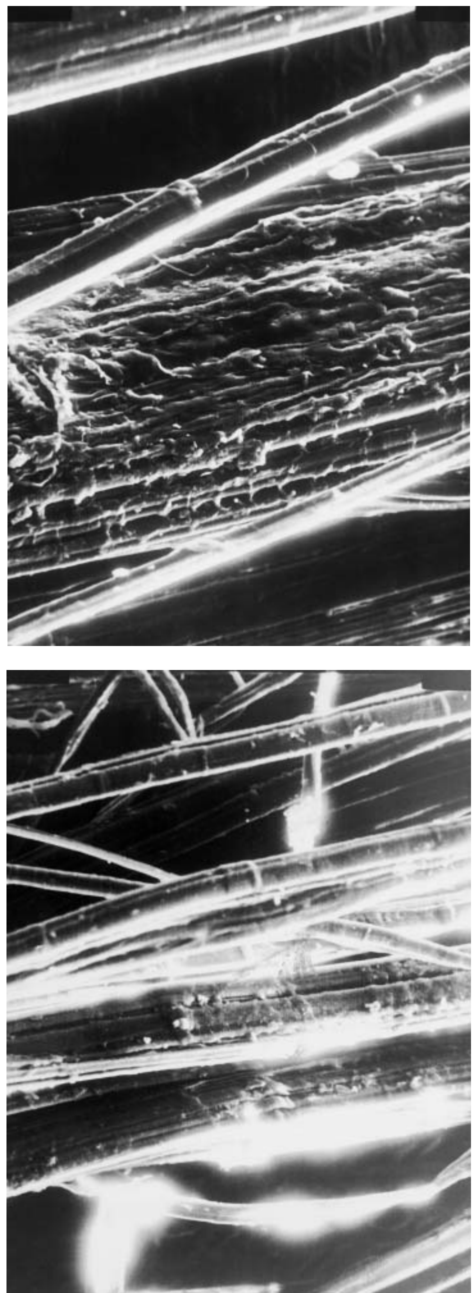

Figure 2. Electron micrographs of: a) natural hemp fibers; b) natural hemp fibers functionalized with β-mercaptopropionic acid.

It was observed that under appropriate storage, in a brown bottle and in a cold room, the sorption and selective properties of hemp sorbent modified with β-mercaptopropionic acid remained unchanged for 2–3 months after preparation. The sulphur content of this sorbent was 0.44 %, corresponding to 0.1375 mmole S $g^{-1}$ of modified hemp.

To describe the $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ sorption characteristics, the experiments were carried out in buffer solutions of $CH_3COOH–CH_3COONa$. The experimental data obtained were analyzed using the Langmuir and Freundlich isotherm models.

It was found that the Langmuir type dependence expressed by Eq. (1):[14]

$$q = k\ c\ q_o / (1 + kc) \qquad (1)$$

where $q$ is the amount of sorbed ion on modified hemp (mmole $g^{-1}$); $k$ is the sorption constant; $c$ is the solution concentration at equilibrium (mole $L^{-1}$ solution) and $q_o$ is the maximum capacity of sorption (mmole $g^{-1}$ modified hemp) between the equilibrium concentrations of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions in the sulphydryl hemp phase and in the aqueous solution phase, respectively, satisfies most of the experimental data. Figure 3 shows the Langmuir equilibrium isotherms for $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ cations retention on the fibrous sorbent under study.

The validity of the Langmuir equation assumes that a monolayer sorption of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ on a surface containing a finite number of sites takes place in the studied systems.

Eq. (1) may be arranged in the linear form (2):

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{kq_0 c} \qquad (2)$$

Hence, a plot of $1/q$ *versus* $1/c$ is linear with the intercept equal to $1/q_0$ and the slope equal to $1/kq_0$. The plots of $1/q$ *versus* $1/c$ for $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ sorption on hemp-SH are shown in Figure 4.

The $q_o$ and $k$ values derived from these linear Langmuir plots are given in Table I.

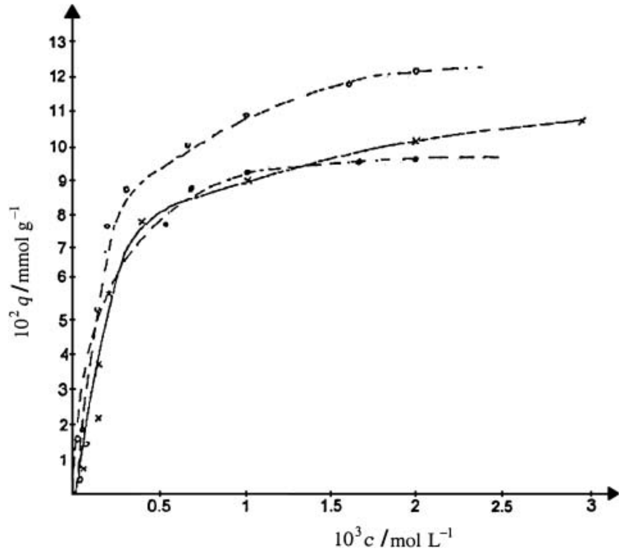


Figure 3. Langmuir isotherms for $Ag^{I}$ (•), $Cd^{II}$ (o) and $Pb^{II}$ (x) ions sorption on sulphydryl hemp fibers.

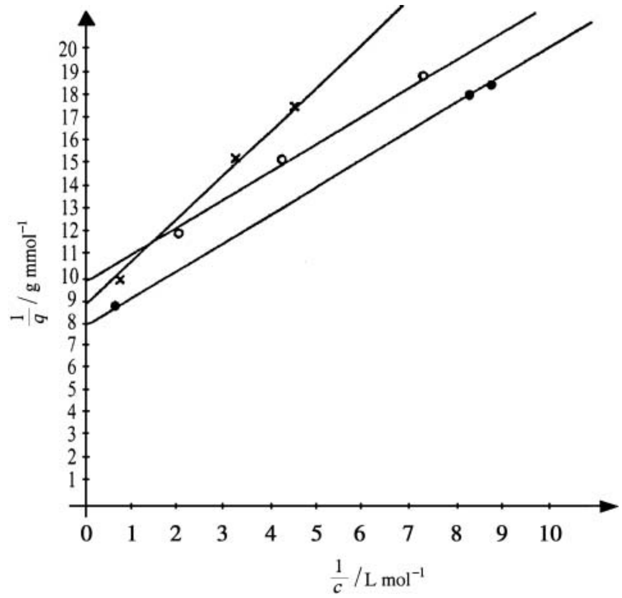


Figure 4. Linear Langmuir plots of $Ag^{I}$ (•), $Cd^{II}$ (o), $Pb^{II}$ (x) cations retention on hemp-SH.

TABLE I. Quantitative description of the sorption systems: hemp-SH-$Ag^{I}$; hemp-SH- $Cd^{II}$ and hemp-SH- $Pb^{II}$ on the basis of the Langmuir isotherm

| Cation | $q_0$/ mmol $g^{-1}$ | | $k$ | $a$ | ΔG | Working range of concentrations |
|---|---|---|---|---|---|---|
| | modified hemp | natural hemp | | | kJ $mol^{-1}$ | μg $mL^{-1}$ |
| $Ag^{I}$ pH = 5.10 | 0.100 | 0.01136 | 8.648 | 0.517 | –5.258 | 4.3–64.7 |
| $Cd^{II}$ pH = 5.75 | 0.125 | 0.02308 | 7.547 | 0.541 | –4.926 | 4.5–67.3 |
| $Pb^{II}$ pH = 3.03 | 0.111 | | 4.687 | 0.507 | –3.765 | 8.3–124.3 |

Also, Table I records the values of the separation factor ($a$) defined by Eq. (3):[10]

$$a = 1 / (1 + kC_0) \quad (3)$$

where $a$ is the separation factor; $k$ is the sorption constant and $C_0$ is the initial cation concentration (μg mL$^{-1}$).

Values of the separation factor express the essential features of Langmuir isotherms, the sorption being favourable for $0 < a < 1$.

Variation of Gibbs free energy ($\Delta G$) for the retention of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions on hemp with the sulphydryl functional groups was determined from the sorption constant with the aid of Eq. (4):

$$\Delta G = -RT \ln k \quad (4)$$

The results shown in Table I indicate that by introducing the sulphydryl functional groups into natural hemp fibers, the capacity of the unconventional cellulosic material in $Ag^{I}$ and $Cd^{II}$ cations retention[3–12] was significantly improved compared to natural hemp. The results show an increase from 0.01136 mmole $Ag^{I}$ / g on natural hemp to 0.100 mmole $Ag^{I}$ / g on hemp-SH and from 0.02308 mmole of $Cd^{II}$ / g on natural hemp to 0.125 mmole $Cd^{II}$ g$^{-1}$ on modified hemp.

By relating the maximum sorption capacity values (Table I) to the sulphur content of the sorbent, it may be concluded that the mechanism of retention is based on the 1:1 complexes formation between the metal ions under study and the sulphydryl groups superficially grafted on hemp fibers. This finding is in good agreement with literature data concerning the sorption of some cations on a resin with thioglycoloyl oxymethylene functional groups.[16]

Referring to the separation factor values, it is obvious from Table I that sulphydryl hemp fiber is a good sorbent for $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions. The obtained values for $\Delta G$ are negative (Table I) and indicate a high affinity of hemp-SH to the tested cations.

*Freundlich Isotherm*

The Freundlich isotherm is represented by Eq. (5):[17]

$$\log X/m = \log K_F + (1/n) \log C_e \quad (5)$$

where $X/m$ is the amount of cations taken up per 1 gram of modified hemp (mg g$^{-1}$); $C_e$ is the cation concentration left in solution at equilibrium (mg mL$^{-1}$); $K_F$ and $n$ are the Freundlich constants relating to all factors affecting the retention process: sorption capacity ($K_F$) and energy of sorption ($n$), respectively.

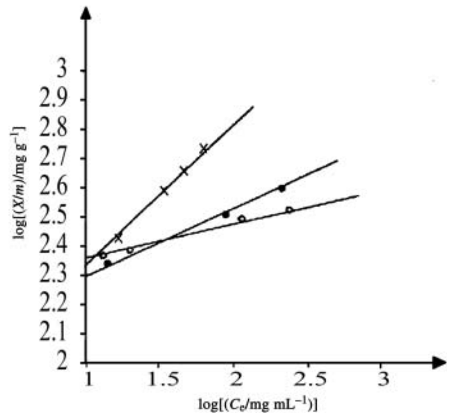


Figure 5. Freundlich plots of $Ag^{I}$ (•), $Cd^{II}$ (o) and $Pb^{II}$ (x) sorption on sulphydryl hemp fibers.

The plots of Eq. (5) for the tested systems are shown in Figure 5.

The linear plots in Figure 5 indicate that sorption of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ cations by complexing with sulphydryl functional groups grafted on natural hemp may also be expressed using the Freundlich isotherm model.

Table II records the $K_F$ and $n$ values derived from the Freundlich plots given in Figure 5.

As can be seen from Table II, in all sorption systems under study $1 < n < 10$. Thus, according to,[17] it may be noticed again that by introducing sulphydryl functional groups into hemp fibers favourable conditions for selective retention of $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ cations were created.

To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. The regression equations of $y = ax + b$ type and the obtained values of the coefficient of correlation, $R^2$, are given in Table III. The results in Ta-

TABLE II. Freundlich constants for $Ag^{I}$, $Cd^{II}$ and $Pb^{II}$ ions sorption on hemp with sulphydryl chelating groups

| | $Ag^{I}$ | $Cd^{II}$ | $Pb^{II}$ |
|---|---|---|---|
| $K_F$ | 2.30 | 2.37 | 2.34 |
| $n$ | 4.68 | 7.76 | 1.71 |

TABLE III. Statistical analysis

| Cation | Langmuir isotherm | | Freundlich isotherm | |
|---|---|---|---|---|
| | Linear regression equation | $R^2$ | Linear regression equation | $R^2$ |
| $Ag^{I}$ | $y = 1.181x + 10.024$ | 0.9999 | $y = 0.151x + 2.237$ | 0.8715 |
| $Cd^{II}$ | $y = 1.215x + 7.845$ | 0.9990 | $y = 0.0721x + 2.335$ | 0.8453 |
| $Pb^{II}$ | $y = 1.853x + 9.034$ | 0.9995 | $y = 0.2221x + 2.285$ | 0.8139 |

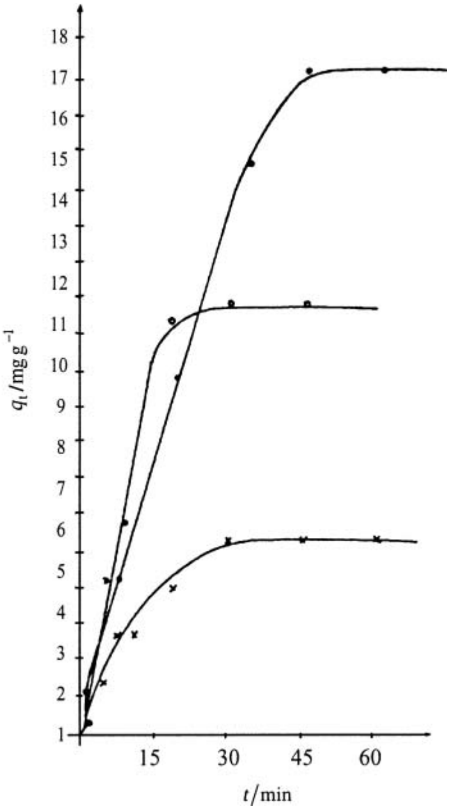


Figure 6. Effect of the stirring time on $Ag^I$ (o), $Cd^{II}$ (x), $Pb^{II}$ (•) retention by hemp-SH.

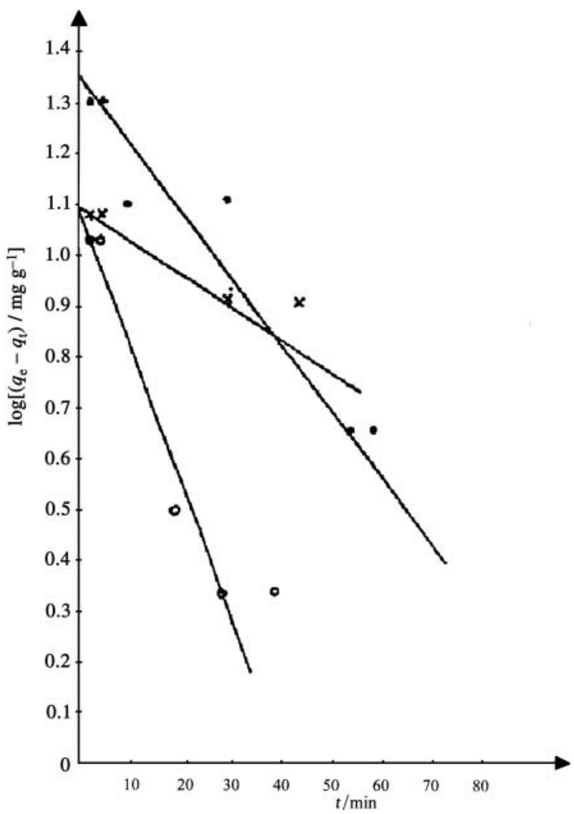


Figure 7. Lagergren plots of $Ag^I$ (o),$Cd^{II}$ (x), $Pb^{II}$ (•) ions sorption on sulphydryl hemp fibers. The respective correlation coefficients, $R^2$, are: 0.7415 for $Ag^I$; 0.8913 for $Cd^{II}$, and 0.9217 for $Pb^{II}$.

ble III allow the conclusion that the obtained data fit better the Langmuir model (higher values for $R^2$).

Figure 6 represents the dependence of the $Ag^I$, $Cd^{II}$ and $Pb^{II}$ retention on hemp-SH on the stirring time of the phases.

On the basis of the kinetic curves in Figure 6, the constant of sorption rate (*k') for Ag*$^I$, $Cd^{II}$ and $Pb^{II}$ was calculated using the Lagergren equation:[17]

$$\log (q_e - q_t) = \log q_e - \frac{k' t}{2.303} \qquad (6)$$

where $q_e$ is the maximum amount of cations taken up per 1 gram of SH-hemp at equilibrium (after 24 h), mg $g^{-1}$; $q_t$ is the amount of cations taken up per 1 gram of SH- hemp at time $t$, mg $g^{-1}$ and $k'$ is the sorption rate constant, $min^{-1}$.

The plots of the Lagergren equation in the sorption systems under study are shown in Figure 7.

Values of $k'$ for $Ag^I$, $Cd^{II}$ and $Pb^{II}$ ions on hemp with sulphydryl groups were determined from the linear plots in Figure 7 as: $5.806\times10^{-2}$, $1.632\times10^{-2}$ and $4.078\times10^{-2}$ $min^{-1}$, respectively. These values reflect the favourable kinetic properties of the chelating sorbent, indicating the feasibility of hemp-SH applications (fibers, filters, fabrics) in environmental management.

In this context, in order to emphasize the practical usefulness of this chelating sorbent, the concentration of trace amounts of $Cd^{II}$ from large volumes of aqueous samples on sulphydryl hemp fibers was carried out under batch conditions.[5] The results of these experiments are very promising for removal of various pollutants from aqueous effluents.

## REFERENCES

1. J. M. Randall, E. Hautala, and G. McDonald, *J. Appl. Polym. Sci.* **22** (1978) 379–389.
2. S. K. Skukla and V. D. Sakhardande, *J. Appl. Polym. Sci.* **42** (1991) 829–835.
3. S. R. Shukla and V. D. Sakhardande, *J. Appl. Polym. Sci.* **41** (1990) 2655–2663.
4. S. R. Shukla and V. D. Sakhardande, *Dyes Pigm. 17* (1991) 101–112.
5. V. M. Gorduza, L. Tofan, D. Suteu, and V. E. Gorduza, *Biomaterials-Biotechnologies-Biocontrol,* Ed. Cermi, Iassy, 2002, pp. 114–140; 505–506.
6. V. M. Gorduza, D. Suteu, and L. Tofan, *Ovidius University Annals of Chemistry* **11** (1) (2000) 120–122.
7. L. Tofan, D. Suteu, M. Vizitiu, and O. Toma, *The Scientific Annals of Al. I. Cuza University* (*Iassy*) **3** (2002) 88–97.
8. C. Paduraru and L. Tofan, *Cellulose Chem. Technol.* **36** (3–4) (2002) 375–380.
9. L. Tofan and C. Paduraru, *Journal of Balkan Ecology* **2** (3) (1999) 106–112.
10. L. Tofan, C. Paduraru, and O. Toma, *The Scientific Annals of the State University from Moldova (Chisinau)* (2001) 204–208.
11. L. Tofan, O. Gherasim, C. Paduraru, and O. Toma, *The Scientific Annals of Al. I. Cuza University* (*Iassy)* **2** (2001) 81–85.

12. L. Tofan and C. Paduraru, *Bull. Polyt. Inst. (Iassy)* **66** (2000) 113–118.
13. Y. H. Lee and J. Mowrer, *Anal. Chim. Acta* **221** (1989) 259–268.
14. I. A. Tihomirov, G. S. Tihonov, E. R. Gofman, and M. I. Bokor, *Zh. Fiz. Chim.* **48** (1974) 1789–1794.
15. G. McKay, H. S. Blair, and A. Findon, *Indian J. Chem.* **28A** (1989) 356–360.
16. E. A. Moyers and J. S. Frits, *Anal. Chem.* **48** (8) (1976) 1117–1124.
17. C. Namasioayan and N. Kanchana, *Chemosfere* **11** (1992) 1691–1705.

## SAŽETAK

### Istraživanje sorpcije $Ag^{I}$, $Cd^{II}$ i $Pb^{II}$ iona na vlaknima konoplje sa sulfhidrilnim skupinama

**Lavinia Tofan i Carmen Paduraru**

Prikazani su i raspravljeni rezultati sustavnih istraživanja sorpcije i kinetičkih svojstava $Ag^{I}$, $Cd^{II}$ i $Pb^{II}$ iona na nekonvencionalnome materijalu pripremljenom uvođenjem sulfhidrilnih funkcionalnih skupina u prirodna vlakna konoplje. Ravnotežne vrijednosti analizirane su primjenom Langmuirovoga i Freundlichovoga isotermnoga modela. Sorpcijski kapacitet monosloja modificirane konoplje pri 18 °C je 10,75, 14,05 i 23,00 mg $g^{-1}$ za srebro, kadmij i olovo. Konstante brzine sorpcije računane prema Lagergrenovoj jednadžbi iznose $5{,}806\times10^{-2}$ $min^{-1}$ za $Ag^{I}$, $1{,}632\times10^{-2}$ $min^{-1}$ za $Cd^{II}$ i $4{,}078\times10^{-2}$ $min^{-1}$ za $Pb^{II}$ ion. Istraživani sustav pruža zanimljive mogućnosti za selektivnu sorpciju različitih zagađivala iz vodenih otopina.