QUALITY IMPROVEMENT OF RECYCLED CHROMIUM IN THE TANNING OPERATION BY FERMENTATION WASTE

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ABSTRACT

The leather industries produce daily large amounts of effluents highly contaminated by chromium salts. The use of sorption phenomenon, especially biosorption on dead residues of microorganisms produced by fermentation industries, can be an economical alternative method to depollute these effluents from heavy toxic metals. In this study we have investigated the adsorption capacity of Cr(III) present in the samples of effluents from a Algeria tannery, by the mycelial by-products of filamentous fungi as *Rhizopus arrhizus*. Efficiency of metal ion recovery from metal-loaded biomass and subsequent regeneration of the biosorbent were also determined. The results show that, at pH 4.8, the biomass was able to adsorb 60 mg/g biomass while precipitation effects augmented these values at higher pH ranges. Adjusting the pH value to about 0 resulted in 95% and 90% recovery of Cr by used H_2SO_4 and HCl respectively. The biomass resulted from desorption processes was able to retain approximately 95% of original adsorption capacity for Cr with sixteenth repeated adsorption and recovery runs. The rate of elimination of the chromium in the effluent of the tannery is about 83% after the sixteenth cycle. The chromium recovered is reused in tannery for preparation of new tanning bath and the obtained results are similar to those obtained by the use of the conventional chromium.

Keywords: biomass, adsorption, chromium, regeneration, tanning, effluent tannery.

1. INTRODUCTION

The transformation of animal skin into hide requires a series of chemical and mechanical treatments. In one of these chemical processes, that is the tanning process, the skin is treated with substances preventing its putrification (Cassano et al., 1990; Cassano et al., 2001). Chromium salts, are the most widely used tanning substances today. Skins that have been tanned with chromium salts present good mechanical resistance, with extraordinary dyeing suitability and better hydrothermic resistance in comparison with the skins treated with vegetal substances (the temperature of a

chromium-tanned hide is 100°C, while a vegetal-tanned hide has a contraction temperature of 75-80°C (Martignore et al., 1974)). Moreover, the chromium salts are characterised by a high rate of penetration into the interfibrillar spaces of the skin: this involves savings and better control of the process.

Unfortunately only a part of the chromium salts (about 60-70%) used in the tanning process reacts with the skins; the residual quantity remains in the tanning exhaust bath that is normally sent to a depuration plant. Here the chromium salts end up into the sludges, creating serious problems for their disposal and/or for their agricultural use (Gauglhofer, 1986).

In Algeria various leather industries recover chromium. The treatment process is based on the precipitation of chromium salt with the addition of basic substances. Particularly, the waste solution originating from tanning and/or retanning processes (containing a quantity of chromium as Cr_2O_3 from 0.3 to 0.8% in weight) is treated with NaOH in order to allow the precipitate to be sent to the filtration plant where panels of sludges containing from 10 to 2% of chromium hydroxide are obtained through filter-pressing. The panels are dissolved again in sulphuric acid and the obtained solution is then adsorbed on fossil flour in order to eliminate the suspended particles and the fat substances. The separation of fossil flour from chromium basic sulphate happens through a final procedure of filter pressing. At the end of the process the final solution contains from 14 to 15% of Cr_2O_3 and is reused in tannery for the preparation of new tanning baths.

A problem observed by tanners is the poor quality of this chromium due to the presence of organic lipolytic components, metals and other impurities (Cassano et al., 1996).

In order to improve the quality of the recycled chromium an alternative to these chemical methods, a study based on the use of microorganisms has been conducted (Tobin et al., 1998; Fourest et al., 1994; Tobin et al., 1984; Aksu, 1990; Nourbash et al., 1994; Volesky et al., 1995). Indeed, a number of microorganisms, including bacteria, yeasts, fungi and micro-algae, were found to be capable of efficiently accumulating heavy metals.

Streptomyces remosus, a filamentous fungus can accumulate chromium. These properties are attributed to the high content of complexing functional groups in their cellular wall (e.g. amino, amide, hydroxyl, carboxyl, sulfhydryl, phosphate radicals) (Brady et al., 1995).

The objectives of this work were to characterize the potential of industrial waste biomass to remove chromium from real leather (tannery) effluent and to investigate subsequent desorption processes to facilitate metal recovery. The re-use of the recovered chromium in the tanning industry was also investigated.

2. MATERIALS AND METHODS

2.1. Effluents

Industrial tanning effluent was supplied by a tanning company (TAMEG ROUIBA ALGERIA) and was stored at 4°C without pre-treatment for a maximum of three months before use. No pH or colour change or precipitation occurred during storage. This effluent was also analysed, the gross characteristics of this effluent are presented in Table 1.

Table 1. Effluent characteristic

Parameter	Value
pH	4.8
B.O.D$_5$ (mg/l)	879
C.O.D (mg/l)	4056
Chromium (III) (g/l)	2.4
Total suspended solids (mg/l)	185

2.2. Biomass preparation

The biomass used is the *streptomycine rimosus*, coming from the SAIDAL-complex manufacturing unit of antibiotics Medea-Algeria. This antibiotic by-product is a mud of Mycelium resulting from the extraction of the fermented gelatine meat-broth for the manufacture of the oxytetracycline.

This biomass underwent a pre-treatment which consists of repeated washing with distilled water until the elimination of the impurities, drying in a drying oven during 48 hours, then crushing and sifting to obtain an easily storable powder of granulometry ranging from 100 to 700 micrometers. Then a chemical treatment is underwent which consists in introducing the dried biomass into a solution of hydroxide sodium of 0.01N concentration. The biomass is maintained in suspension by agitation during 30 min at ambient temperature, repeatedly filtered and washed with distilled water then dried in the drying oven at 50°C during 2 hours.

The physical properties of the biosorbent are shown in Table 2.

Table 2. The physical characteristics of the biomass

	NaOH-treated biomass
Particle size d_p (µm)	50-160
Humidity (%)	4.4
ρ_{app} (g cm^{-3})	0.41
S (m^{-1})[a]	418
S_p (m^2 g^{-1})[a]	0.14
Zeta potential (Volt)	-0.072

[a] An average value of d_p was used for calculation.

2.3. Chromium uptake

Serial dilutions of the tanning effluent were prepared using deionised distilled water to give solutions ranging in concentration from full strength to 1 in 20 dilutions. Aliquots of 100 ml were contacted with 0.3 g quantities of a biomass. Samples were filtered and the filtrates were analysed for remaining metals using a Perkin Elmer 2380 atomic absorption spectrophometer. The determination of the capacity of absorption is done through the evaluation of the residual concentration of metal with a regular interval of time. The isotherm of absorption is determined by the measurement of the concentration of chromium in balance.

2.4. Desorption studies

After biosorption experiments, the solution were filtered, with bases of polystyrene filter mesh of pore size 36 um. The cake (the metal-loaded biomass) obtained was rinsed and immersed in the flask containing of 50 ml chlorhydrique or sulphuric acid at different concentrations. After gentle agitation, the biosorbent suspensions were centrifuged, and the metal concentration in the supernatant was determined as described above, this operation is repeated successively until a total desorption This operation is repeated successively until total desorption of the chromium. The regenerated biosorbents were again suspends in aliquots of 100 ml (tanning effluent) for the next adsorption/desorption steps described above were repeated five times.

## 2.5. Tanning operation with chromium extracted with different acids

The chromium desorbed with sulphuric acid after the addition of the sodium carbonate to obtain a liquor of alkalinity of about 33% basicity was tested as such in the tanning operation on a sample of pickled hide with standard tanning methods (Jullien et al., 1998). The leather samples tanned with the chromium desorbed were compared by

means of some chemical and physical tests on both the groups of skins using control samples obtained with standard tanning methods.

3. RESULTS AND DISCUSSION

3.1. Adsorption mechanism

Equilibrium absorption isotherms of Cr(III) by dead biomass of *Streptomyces remosus* at pH 4.8 shown in Figure 1. Absorption isotherms represent the equilibrium distribution of metal ions between the aqueous and solid phases, when the concentration increases. The curve is concave to the x-axis which is characteristic of microbial metal binding although saturation uptake levels were not attained at the equilibrium solution concentrations involved (Tobin et al., 1998).
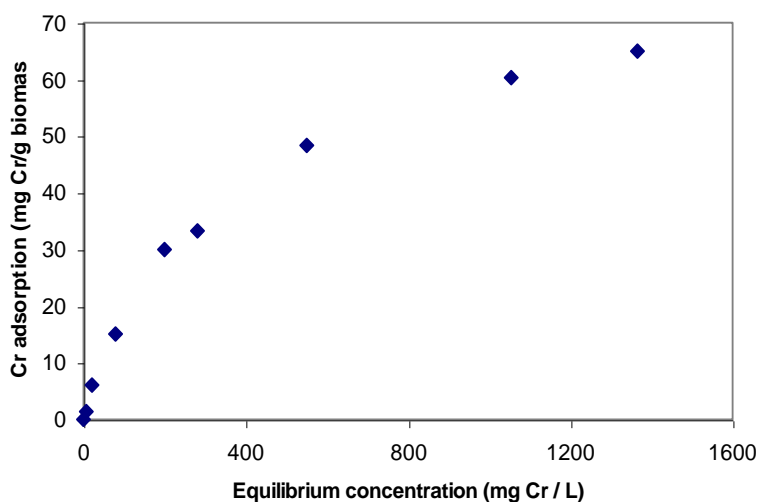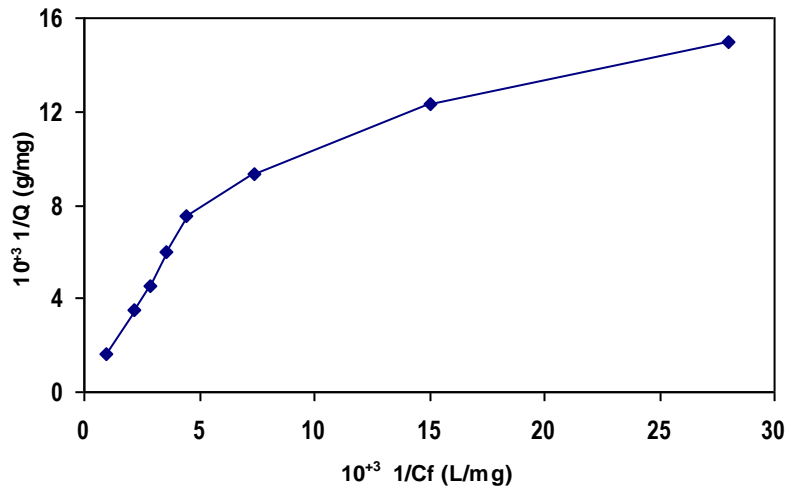

Fig. 1 Equilibrium sorption isotherm of Cr by Rhizopus arrhizus during 5 h
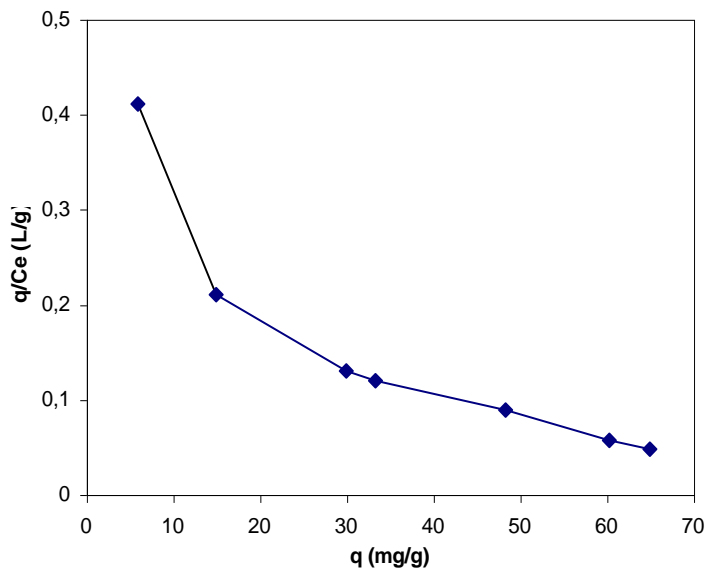(Biomass concentration = 3g/l; $pH_{initial}$ = 4.8; T = 20°C)

Moreover, uptake data have frequently been successfully fitted to the Langmuir absorption model and a simple monolayer, non-interactive binding mechanism proposed. When the data were transformed to the reciprocal Langmuir format (Langmuir, 1918), a clearly non-linear plot resulted as seen in Figure 2. This non-conformity to idealized Langmuir behaviour may be interpreted as indicating complex absorption processes involving multilayer, interactive or multiple site type binding or some combination of these phenomena.

The data were further transformed to the Scatchard format (Scatchard, 1949) as shown in Figure 3, which also resulted in a clearly non-linear plot. In this study the highly curved nature of the Scatchard plot indicates the existence of the multiple types binding sites in the biomass and/or multiple forms of chromium in solution. Moreover,

the authors (Bases et al., 1976; Kratochvil, 2002) show that chromium may exist in the form of Cr(III), $Cr(OH)^{+2}$, $CrSO_4^+$, $Cr_2((OH)_2(SO_4))^{2+}$, $CrOHSO_4$, $Cr_2(OH)_2(SO_4)_2$.

Fig. 2 Langmuir transformation of equilibrium sorption isotherm of Cr by Rhizopus arrhizus (Biomass concentration = 3g/l; $pH_{initial}$ = 4.8; T = 20°C)

Fig. 3 Scatchard transformation of equilibrium sorption isotherm of Cr by Rhizopus arrhizus (Biomass concentration = 3g/l; $pH_{initial}$ = 4.8; T = 20°C)

3.2. Effect of initial pH on Chromium adsorption

The effect of pH on the adsorption capacity of chromium with biomass of *streptomycine rimosus* was identified, then the pH value was raised from 1 to 4.8, the adsorption capacity was enhanced significantly from 27 to 64 mg/g biomass.

Absorption studies at pH 5.5 and 7.0 marked precipitation effects augmented the biosorption removal of chromium from solution resulting in apparent sequestration levels of in excess of 93 and 133 mg/g respectively as illustrated in figure 4. As can be seen in the figure, when the precipitation component is subtracted the net biosorption values are in good agreement with each other and those observed at pH 4.8.

The fact that sorption potential is nit affected by precipitation is of potential industrial significance. Metal-bearing effluent, such as that from tanneries (Stein et al., 1994) frequently contains residual salts and precipitation following primary treatment. The optimal pH for adsorption of chromium by mycelia by-products of *streptomycine rimosus* was around 4.8.
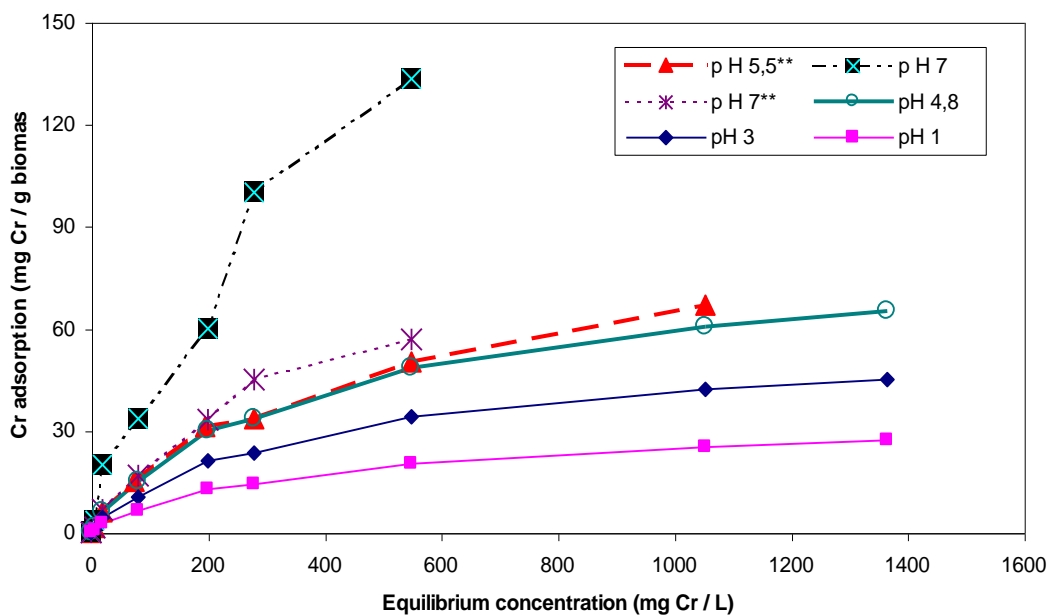

Fig. 4. Effect of pH and influence of precipitation on uptake (** indicates where precipitations effects have been subtracted)

3.3. Chromium desorption

Effects of decreasing pH. Chromium desorption increased with decreasing desorption agents pH (including HCl and H_2SO_4) to a maximum value of ca. 95% at approximately zero pH. At pH values of 1.0 and 2.0 only ca. 66 and 51% chromium was recovered respectively. Variation of the acid: (Chlorhydrique or Sulphuric acid) caused non-difference in desorption over the experimental range investigated as shown in Figure 5.
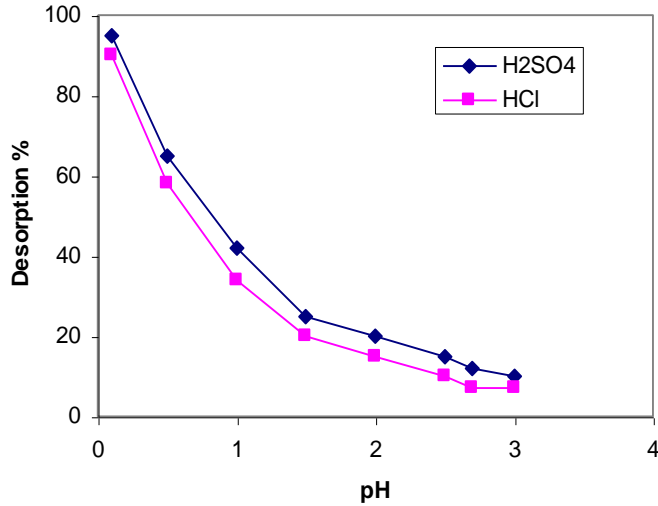
Fig. 5. Effect of desorption agents (H_2SO_4, HCl) pH on desorption efficiency

The kinetics of the desorption of Cr from the chromium metal loaded biomass is demonstrated in Fig. 6. It can clearly be seen that metals desorbed very rapidly, and the desorption reached equilibrium within 12 min. The desorption efficiency was around 95% (H_2SO_4 desorption agent), 90% (HCl desorption agent) for chromium recovered.
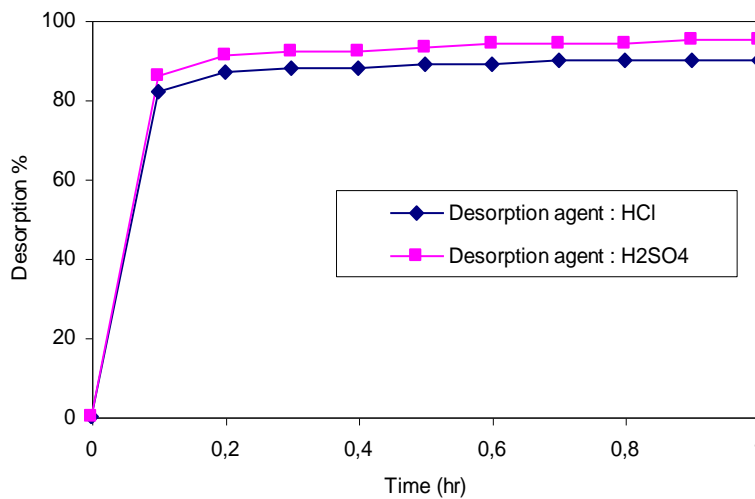
Fig. 6. Time-course profiles for the desorption of chromium from chromium-loaded biomass

Increasing acid concentrations. At each eluant concentration the percentage desorbed chromium was essentially independent of chromium loading on the biomass as shown in Figure 7. Desorption stages with increasing acid concentrations resulted in a recovery exceeding 80% of the isolated chromium although the use of 2 N acid caused visible alteration of the biomass structure.
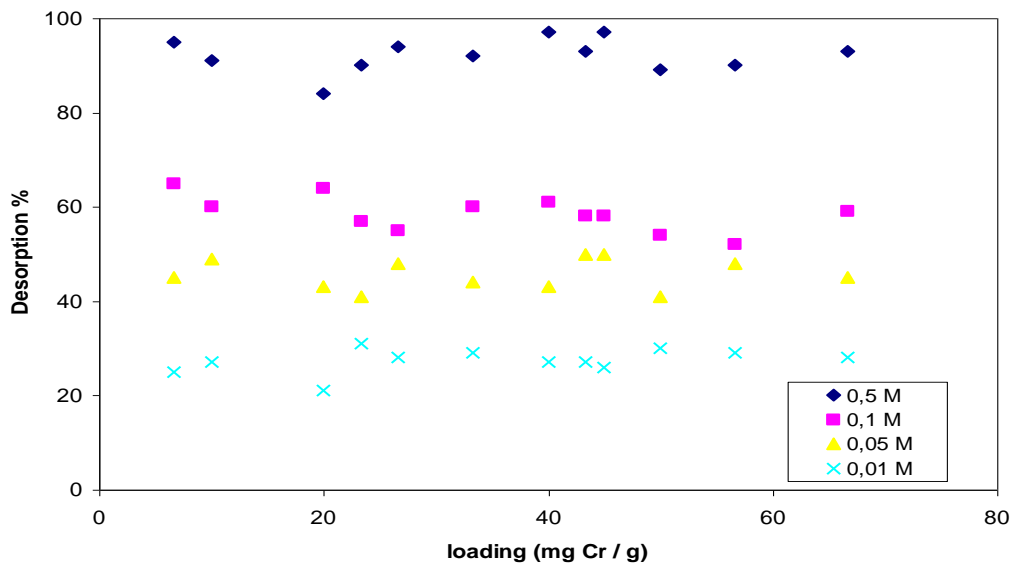
Fig. 7. Cumulative desorption efficiency with successive treatments of increasing eluant (H$_2$SO$_4$) concentration

3.4. Adsorption/desorption cycles

Repeated adsorption/desorption (A/D) operations were performed to examine the reusability and metal recovery efficiency of the biomass. As shown in Table 3, with sixteen A/D cycles, the Cr adsorption capacity of the biomass decreased slightly from 60 mg/g died biomass (cycle = 1) to about 27.8 mg/g died biomass (cycle = 16), and for all cycles nearly 94% of adsorbed Cr was recovered with H$_2$SO$_4$ (1N) - driven desorption.

The concentration of chromium in the effluent of the tannery passes from 2, 4 g/l to 0, 38 g/l at the end of the sixteenth cycle, what corresponds to a rate of elimination of chromium in the effluent of the tannery of 83.5%, as well as the cumulative concentration of the chromium desorbed in the sulphuric acid at 1 N is about 1.906 g/l. The concentration of the chromium in the sewage of the tannery passes from 2.4 g/l to 0.38 g/l at the end of sixteenth cycle what corresponds has a rate of elimination of the chromium in the effluent of the tannery of 83.5%.

Table 3 Adsorption/ desorption cycles for Cr with biomass.
The initial concentration of Cr at the first cycle was 2.4 g/litre; (**Biomass concentration = 3g/l; pHi (adsorption) = 4.8; pH (desorption) = 0; T = 20°C)**

Number of cycles	Adsorption					Desorption		
	Qads (mg/g) **(a)**	Cads (mg/l) **(b)**	Cc (mg/l) **(c)**	C_R (mg/l) **(d)**	% Elim **(e)**	Qdes (mg/g) **(f)**	Cdes (mg/l) **(g)**	Cdes-c (mg/l) **(h)**
1	60.0	180.0	180.0	2220	7.5	57	171.0	171
2	57.0	171.0	351.0	2049	14.6	54.1	162.4	333
3	54.5	163.2	514.2	1885	21.4	51.4	154.3	487
4	51.4	154.3	668.5	1731	27.8	48.8	146.6	633
5	48.8	146.6	815.1	1584	33.9	46.4	139.2	772
6	46.4	139.2	954.3	1445	39.7	44.1	132.3	904
7	44.1	132.3	1086.6	1313	45.2	41.9	125.7	1029
8	40.9	125.7	1212.3	1187	50.5	39.8	119.4	1148
9	39.8	119.4	1331.7	1068	55.4	37.8	113.4	1261
10	37.8	113.4	1445.1	954	60.2	35.9	105.0	1366
11	35.9	107.7	1552.8	847	64.7	34.1	102.3	1468
12	34.1	102.3	1655.2	744	68.9	32.4	97.2	1565
13	32.4	97.2	1752.4	647	73.0	30	92.4	1657
14	30.8	92.4	1844.8	555	76.8	29.2	87.6	1744
15	29.2	87.7	1932.6	467	80.5	27.7	83.3	1827
16	27.7	83.3	2015.1	383	83.5	26.4	79.2	1906

(a) Chromium uptake (mg/g biomass)
(b) Chromium uptake (mg/L effluent)
(c) Cumulative uptake over 14 successive cycles (mg/L effluent)
(d) Residual chromium ion concentration in effluent over 14 successive cycles (mg/L)
(e) Cumulative percentage elimination (percentage adsorption) over 14 successive cycles
(f) Chromium quantity desorption by utilising H_2SO_4 desorption agent (mg/g biomass)
(g) Chromium quantity desorption in H_2SO_4 desorption agent (mg/L)
(h) Cumulative desorption in H_2SO_4 desorption agent over 14 successive cycles (mg/L)

3.5. The re-use of extracted chromium in the tanning operation

The chromium desorbed with sulphuric acid (1N) was adjusted through the addition of NaOH (solution at 50%) to get one liqueur of tanning has a basicity of the order of 33%. The final product was employed in tannery to perform experimental tanning essays on a sample of pickled hide.

For tanning tests, we have used two samples of pickled hide (named Sample A and B). Sample A was tanned with the chromium desorbed with sulphuric acid (1N), while Sample B was tanned with the conventional method which envisages the use of pure chromium basic sulphate.

In Tables 4 and 5, the results of the chemical and physical analyses carried out on the leather samples are reported. They show:

- Higher values of tensile strength and tear strength for the skins tanned with the extracted product
- The same content of chromium oxide in both samples;
- Contraction temperature higher than 105°C for the skins tanned with the extracted product

These results are quite satisfying for use at industrial scale.

Table 4. Physical analyses on leather samples tanned with the recovered highly concentrated chromium solution and with a standard chromium solution

Parameter	Sample A	Sample B
Tensile strength, kg/mm^2	2.16	2.2
Breaking load, kg	54	50
Alongation at break, %	32	31
Tear strength, kg	3.6	3.8
Tear load, kg	8.8	8.6
Contraction temperature, °C	>105	>105

Table 5. Chemical analyses on leather samples tanned with the recovered highly concentrated chromium solution (9.2% as Cr2O3) and with a standard chromium solution

Parameter, %	Sample A	Sample B
Humidity and volatile substances at 102°C	20	21.2
Total sulphate ash at 800°C	10	9.8
Chromium oxide	3.9	3.7
Total nitrogen	10.5	11.5
Leather substance	58.3	60.5

CONCLUSION

The biosorbent which was investigated in this study (*streptomycine rimosus*) was capable of adsorbing chromium from tannery effluent; the optimal pH for adsorption of chromium by mycelial by-products of *streptomycine rimosus* was around 4.8. The insensitivity of the biosorption process to high levels of precipitates underlines the potential for application in final/polishing or co treatment systems. The desorption

efficiency was around 95% (H_2SO_4 desorption agent), 90% (HCl desorption agent) for chromium recovered.

Repeated adsorption/desorption (A/D) operations made it possible to lower the concentration of the chromium in the sewage of the tannery from 2.4 g/l to 0.38 g/l at the end of sixteenth cycle what corresponds has a rate of elimination of the chromium in the effluent of the tannery of 83.5%. Physical and chemical proprieties of obtained leather through tanning of chrome desorbed with sulphuric acid (1N) are equivalent to those obtained when using pure sulphated chrome. The method is potentially attractive to the tanning industry and it will prevent environmental pollution by chromium contained in leather waste shavings.

REFERENCES

Bases, C.F. and Menser, R.E. (1976) The hydrolysis of cations. John Wiley and Sons, New York.

Brad, Y.J.M. and Tobin, J.M. (1995) Binding of hard and soft metal ions to *Rhizopus arrhizus* biomass, *Enzyme. Micob. Technol*. **17** 791-796.

Cassano, A., Molinari, R. and Drioli, E. (1990) Saving of water and chemicals in tanning industry by membrane processes, *Wat. Sci. Tech*. **40** 443-450.

Cassano, A., Molinari, R., Romano, M. and Drioli, E. (2001) Treatment of aqueous effluents of the leather industry by membrane processes, *Journal of Membrane Science* **182** 11-126.

Cassano, A., Molinari, R., Drioli, E. and Bertolutti, C. (1990) Quality improvement of recycled chromium in the tanning operation by membrane processes. *Desalination* **108** 193-203.

Fourest, E., Canal, C. and Roux, J.C. (1994) Improvement of heavy metals biosorption by mycelial dead biomasses *Rhizopus arrhizus, Mucor miehei, Penicillium chrysogenum*: pH control and cationic activation, *FEMS Microbiol. Rev*. **14** 325-332.

Gauglhofer, J. (1986) Environmental aspects of tanning with chromium, *J. Soc. Leather Technologists Chemists* **70**(1) 11-16.

Julien, I. and Gavend, G. (1998) Le cuir origine et fabrication. Document pedagogique du center technique du cuir.

Kratochvil, D., Pimentel, P.F. and Volesky, B. (2002) Removal of trivalent chromium by seaweed biosorbent. Private communication

Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* **40** 1361-1403.

Martignore, C. and Conceria, P. (1974) Ed, Editrice Universitaria Levroyyo e Bella, Torino.

Nourbash, M., Sag,Y., Ozer, D., Aksu, Z., Kustal, T. and Caglar, A. (1994) A comparative study of various biosorbents for Chromium(VI) ions from industrial waste water. *Process Biochem.* **29** 1-5.

Scatchard, D. (1949) The attraction of proteins for small molecules and ions, Ann. N.Y. Acad. Sci. **51** 145-149.

Stein, K. and Schwedt, G. (1994) Speciation of chromium in the waste water from a tannery. *Frenius J. Anal. Chem.* **350** 38-43.

Tobin, J.M. and Roux, J.C. (1998) Mucor biosorbent for chromium removal from tanning effluent, *Wat. Res.* **32** 1407-1416.

Tobin, J.M., Cooper, D.G. and Neufeld, R.J. (1984) Uptake of metal ions by *Rhizopus arrhizus* biomass, *Appl. Environ. Microbiol.* **47** 821-824.

Aksu, Z., Sag, Y. and Kustal, T. (1990) A comparative study of the adsorption of chromium(VI) ionsto C. vulgaris and Z. ramigera. *Environ. Technol.* **11** 33-40.

Volesky, B. and Holan, Z.R. Biosorption of heavy metals. *Biotechnol. Prog.* **11** 235-250.