

Use of chitosan for chromium removal from exhausted tanning baths

Raffaele Cesaro, Massimiliano Fabbricino, Rosa Lanzetta, Anna Mancino, Biagio Naviglio, Michelangelo Parrilli, Roberto Sartorio, Michele Tomaselli and Gelsomina Tortora

ABSTRACT

A novel approach, based on chitosan heavy-metal sequestering ability, is proposed for chromium(III) removal from spent tanning liquor. Experimental results, obtained at lab-scale using real wastewater, are presented and discussed. Resulting efficiencies are extremely high, and strongly dependent on chitosan dose and pH value. Comparative analyses with other polysaccharides is also carried out showing that amine groups are more efficient than carboxyl and sulphate ones. Chromium recovery from sorption complexes and chitosan regeneration is finally proposed to optimize the whole process.

Key words | chitosan, chromium sorption, polysaccharides, tanning industry, wastewater

Raffaele Cesaro
Massimiliano Fabbricino
Department of Hydraulic and Environmental
Engineering Girolamo Ippolito,
University of Naples Federico II,
via Claudio 21, 80125,
Naples,
Italy
E-mail: fabbrici@unina.it

Rosa Lanzetta
Anna Mancino
Michelangelo Parrilli
Department of Organic Chemistry and
Biochemistry,
University of Naples Federico II,
Via Cintia 4, 80126 Naples,
Italy

Roberto Sartorio
Department of Chemistry,
University of Naples Federico II,
Via Cintia 4, 80126 Naples,
Italy

Biagio Naviglio
Michele Tomaselli
Gelsomina Tortora
Stazione Sperimentale per l'Industria delle Pelli e
delle Materie Concianti,
Via Poggioreale,
Naples,
Italy

INTRODUCTION

Chromium(III) is the most abundant metal present in the wastewater produced by tanning industry. The tanning process, in fact, converts the putrescible animal hides into a stable material which is resistant to microbial attack, using Cr^{3+} tanning salts, usually $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Covington 1997). As the process is carried out with salt excess, about 30–40% in mass of Cr^{+3} does not react with the hide and is discharged in the form of spent tanning liquor. Due to the high chromium(III) content, the disposal of this liquor represents a serious environmental problem. The removal of chromium from aqueous solutions is an hot topic, as shown

by the increasing number of researches aimed at finding efficient chromium(III)-sequestering materials (Volesky & Holan 1995; Pandey *et al.* 1996; Araújo & Teixeira 1997; Tobin & Roux 1998; Bailey *et al.* 1999; Aliane *et al.* 2001; Dantas *et al.* 2001; Gupta *et al.* 2001; Kim 2003; Pandey *et al.* 2003). Interesting results seem to be related to the use of carbohydrate-biomasses (Volesky & Holan 1995; Bailey *et al.* 1999) and alginates (Araújo & Teixeira 1997; Pandey *et al.* 2003), as sequestering agents. In order to extend the investigation on the metal sequestering ability of other polysaccharides, the paper presents the results obtained

using chitosan to remove chromium(III) from a rich exhausted tanning bath.

Chitosan is a linear polysaccharide built of 4-linked- β -2-amino-2-deoxy-glucopyranose residues, some of which (<8%) are N-acetylated. It is a natural polysaccharide found in some fungi, but its main source derives from the N-deacetylation of chitin, the most abundant natural polysaccharide after cellulose, which is extracted from crustacean material. Chitosan is a well known heavy-metal sequestering polysaccharide (Muzzarelli & Rocchetti 1974) and its ability had been tested also for chromium sorption (Masri *et al.* 1974; Muzzarelli & Rocchetti 1974; Eiden *et al.* 1980; Maruca *et al.* 1982) but, to our knowledge, never directly on exhausted tanning baths, as proposed in the paper.

To further investigate the convenience of chitosan use for tanning wastewater treatment, its performances are compared with those obtained using other two polysaccharides, carrageen and pectin, and, finally, the possibility of chromium recovery from chromium-chitosan complexes is investigated.

MATERIAL AND METHODS

All experiments were performed on 5 ml samples of wastewater collected from a tanning industry in Naples Area (Italy). At the beginning of the test, varying amounts of chitosan, ranging from 10 to 200 mg were added to the samples. Each of them was stirred with a magnetic equipment, at room temperature, for 24 h, and centrifuged at 3,000 rpm at the end of the test. The supernatant was analyzed for residual chromium concentration detection: metal concentration was determined using a Plasma Atomic Emission Spectrometer (ICP-AES).

Chitosan-chromium(III) complexes collected after centrifugation were used for chitosan regeneration tests: these latter were performed in acidic conditions using a mixture of concentrated sulphuric acid and water, testing two different volumetric ratio: 1:1 and 3:7.

To compare the performances of chitosan with other polysaccharides, some experiments were performed using carrageen and pectin instead of chitosan, following the identical procedure over-described.

All polysaccharides, including chitosan, were purchased by Fluka (Italy) and used without further purification

RESULTS AND DISCUSSION

Table 1 reports Cr(III) concentration, expressed as g· or l^{-1} of Cr_2O_3 , in the exhausted tanning bath, after treatment with chitosan, carrageen, and pectin. As it can be easily deduced, although pectin was the most efficient material at lower tested concentrations, only chitosan was able to remove completely chromium(III) from the exhausted tanning bath. This suggests that amine groups (chitosan) are more efficient than carboxyl (pectin) and sulphate (carrageenan) ones in sequestering chromium.

Figure 1 reports the amount of added chitosan for all performed experiments *versus* the equilibrium Cr^{3+} molar concentration. The data can be fitted to a six degree polynomial, having the following equation:

$$c = -2 \cdot e^{-13} W^6 + 6 \cdot e^{-11} W^5 - 5 \cdot e^{-9} W^4 - 2 \cdot e^{-7} W^3 + 2 \cdot e^5 W^2 - 0.0008 \cdot W + 0.1497 \quad (1)$$

Table 1 | Chromium concentration in the centrifuged wastewater as function of the added polysaccharide

Added amount (mg)	Cr ⁺³ (g· or l^{-1} as Cr_2O_3)		
	Chitosan	Carrageenan	Pectin
0	8.0	8.0	8.0
10	7.6	8.0	7.4
20	7.6	8.0	5.1
30	7.4	7.9	4.6
40	7.3	7.7	4.8
50	6.8	7.6	4.2
60	6.3	7.6	4.2
70	5.9	7.2	3.7
80	4.2	6.8	3.4
90	3.7	6.7	3.9
100	2.3	6.4	2.8
110	1.4	6.1	2.8
120	0.6	5.6	2.8
130	0.2	5.6	2.8
140	0.0	4.9	3.2
150	0.0	4.9	2.7

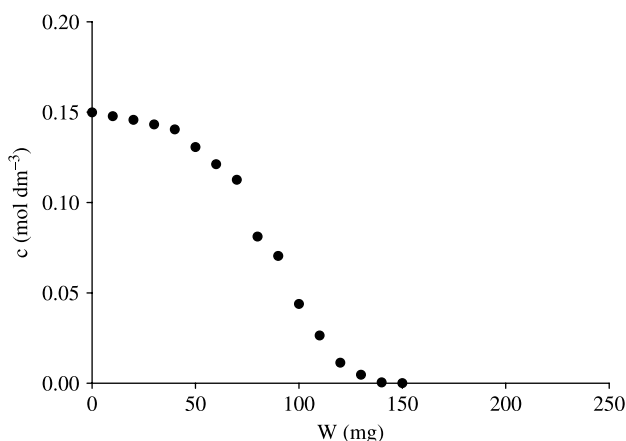


Figure 1 | Chromium residual concentration at the end of the chitosan extraction tests.

where: $c = \text{Cr}^{3+}$ molar concentration after chitosan addition ($\text{mol}\cdot\text{dm}^{-3}$); W = amount of added chitosan (mg).

The polynomial degree was chosen as the lowest one that gives a statistical distribution of the residues as a function of the independent variable. This preliminary fitting was necessary to avoid large errors in the following analysis involving numerical derivatives. Using the fitting equation it was computed the ratio, θ , between the amount of removed chromium and the amount of added chitosan:

$$\theta = \frac{V \cdot (c^0 - c)}{W} \quad (2)$$

where: V = volume of the original solution; c^0 = initial Cr^{3+} molar concentration.

The ratio θ is plotted, in Figure 2, as a function of the effluent chromium(III) concentration c . From the obtained

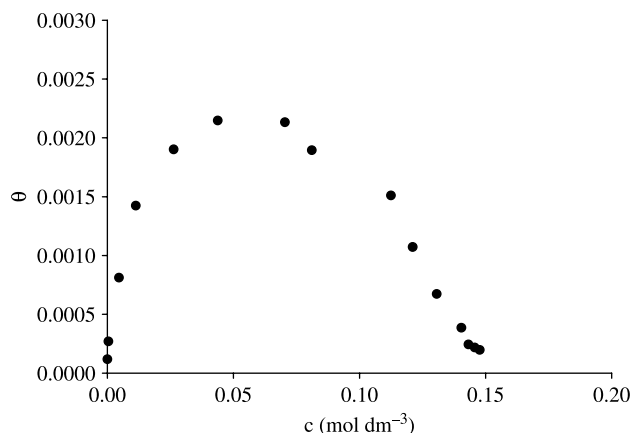


Figure 2 | θ trend as a function of extraction effluent chromium concentration c .

profile it appears that the chitosan-chromium interactions are poorer at higher molar concentration. Moreover, for $c < 0.06\text{--}0.07 \text{ mol}\cdot\text{dm}^{-3}$ the trend is consistent with a Langmuir-type absorption isotherm.

In order to understand this behavior, it has to be considered that the mechanisms responsible for metal sorption include several processes, such as precipitation, deposition of metal aggregate, ion-exchange and complexation (Guibal et al. 1995). The predominant mechanism is function not only of the absorbent structure, but also of other parameters, such as pH values. During performed experiments pH values varied due to the amount of added chitosan, as shown in Figure 3. It is interesting to observe that the pH trend has an S shape with an inflection point correspondent to $\text{pH} \cong 5$, typical of titration curves. The Langmuir-type adsorption isotherm trend corresponds to pH values higher than $\text{pH} \cong 5$, while poor chitosan-interaction are observed for lower values. The increase of pH medium by adding chitosan is opposite to what occurs when increasing amounts of metals are added to an acidic solution of chitosan, as shown by the following symbolic reaction (Rhazi et al. 2002), foreseeing a pH decrease as consequence of the metallic ion fixation to the chitosan molecule:



It has to be added that during the performed experiments pH increase was due not only to the neutralization

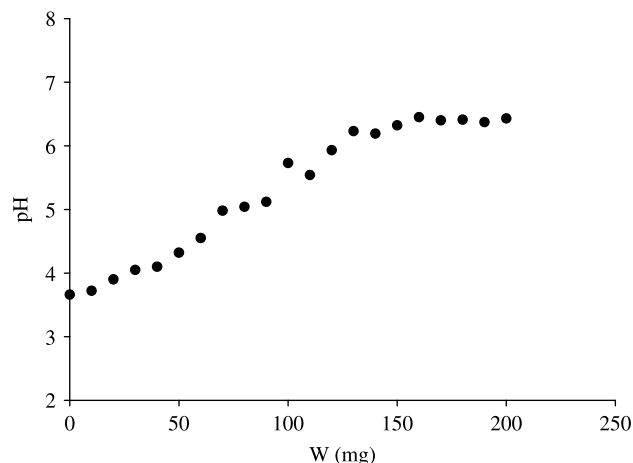


Figure 3 | pH variation during chitosan extraction experiment.

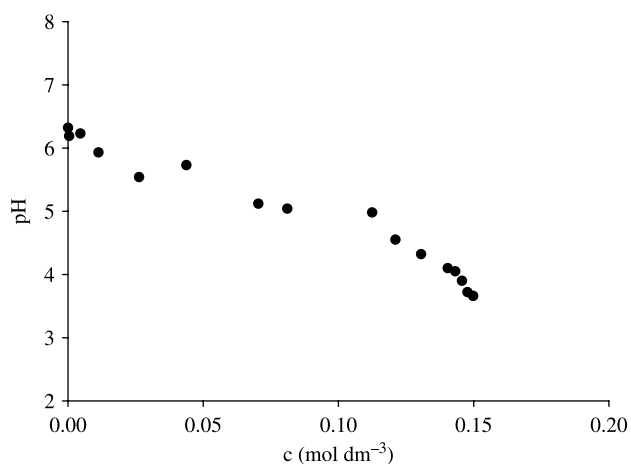


Figure 4 | pH trend as a function of extraction effluent chromium concentration c .

of the solution caused by the continuous addition of the polysaccharides, but also by hydroxyl groups which co-ordinate the chromium species in solution. It is known that the active chromium(III) species in a tanning baths are represented by a complex mixture of sulphated chromium hydrolytic oligomers, such as the dimer $\text{Cr}_2[(\text{H}_2\text{O})_8(\text{OH}^-)_2]^{4+}$, the trimer $\text{Cr}_3[(\text{H}_2\text{O})_9(\text{OH}^-)_4]^{5+}$, the tetramer $\text{Cr}_4\text{O}_2[(\text{H}_2\text{O})_{12}(\text{OH}^-)_4]^{4+}$ and longer oligomers with different tanning ability (Gotsis *et al.* 1992; Rao *et al.* 1999). Similar species with a lower collagen affinity are also founded in the spent tanning bath (Rao *et al.* 1999), therefore when chromium binds chitosan, the hydroxyl groups which are free, neutralize the solution acidity.

Figure 4 indicates that the effluent concentration of Cr^{3+} increases at lower pH. This can be explained considering the protonation of chitosan amine, which occurs at low pH and reduces the chitosan capacity to coordinate chromium(III).

As previously said the treatment process was completed by preliminary tests aimed at studying the possibility of chromium recovery after precipitation with chitosan. According to the relative content of sulphuric acid and water used in the treatment of the chitosan-chromium(III) complexes obtained after centrifugation, different results were obtained. Using a 1:1 volumetric ratio, the complete precipitate dissolution was reached due to the salification of the amine group, whereas with a less acid mixture (3:7) only the decomplexation was

obtained. Under these conditions chitosan remained insoluble and could be removed by centrifugation, in order to use it again for further chromium precipitations, while soluble Cr^{3+} remained in the supernatant liquid, being potentially available for a new tanning bath.

CONCLUSIONS

Pollution caused by tanning industry is greatly related to the concentration of chromium(III) in the spent tanning liquor. In the paper a novel approach for Cr^{3+} removal from tanning wastewater has been proposed, based on the use of chitosan as sequestering agent. Obtained results showed that chitosan is able to complete remove chromium(III) from the spent tanning bath, but the performances of the process are strongly dependent on pH values. Particularly chitosan is a less efficient chromium sequester at lower pH because in this case the protonation equilibrium of chitosan amine is more shifted towards the protonated form, and therefore chitosan is less able to coordinate chromium. Preliminary tests showed that it is possible to complete dissolve the chitosan-chromium complex, whenever a strong acid mixture of sulphuric acid in water is used to treat the precipitate, and therefore chromium recovery and chitosan regeneration can be obtained from the sludge of the wastewater treatment process.

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