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Chromium removal from tannery wastewater using ground shrimp shells

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ABSTRACT

Crustacean shells contain high levels of chitin, a biopolymer that can be used to chelate metal ions. This study investigated the use of crustacean shells for chromium removal from tannery wastewater. Preliminary experiments aimed to determine whether chromium removal was due to adsorption by the carbohydrate's chemical groups or to formation of insoluble chromium hydroxide due to the pH increase from addition of the polysaccharide to the wastewater. These experiments were performed using synthetic wastewater and commercial chitosan, a chemical compound obtained by chitin deacetylation. Subsequent experiments, carried out using tannery wastewater, were performed to determine whether chromium could be recovered from the sludge. Finally, different amounts of ground shrimp shells from fishery waste were used to remove chromium from tannery wastewater. The results showed that chromium removal was mediated primarily by adsorption and that chromium recovery from sludge was possible at very low pH. Ground shrimp shells removed chromium more effectively than commercial chitosan due to the combination of precipitation and adsorption processes.

Keywords: Adsorption; Chitin; Chromium; Wastewater; Tanneries

1. Introduction

Chromium sulphate is the compound that is most commonly used to stabilize animal hides, and the exhausted bath produced by leather tanneries is rich in chromium. Due to the large excess of salt used in the tanning process [1], it is not rare to find chromium III [Cr(III)] concentrations of several thousands milligrams per liter in spent tanning baths. Such levels are at least three orders of magnitude greater than the concentration allowed for discharge to the environment by regulatory laws in the European Union and elsewhere. Chromium removal thus represents the main concern of tannery wastewater treatment. Precipitation processes are frequently used to remove chromium [2]. Because chromium hydroxide is insoluble, the chromium concentration in wastewater can be drastically reduced through the addition of lime. Lime treatment is quite inexpensive, but the process must be carried out carefully. Due to the colloidal state of precipitated compounds, wastewater must be sufficiently neutralized, coagulated, and flocculated for efficient removal [3].

Adsorption processes offer an interesting alternative to precipitation. In order to be competitive with lime, materials used for adsorption must be inexpensive, but many adsorption materials, such as activated carbon [4], are very costly. Recently, efforts have focused on testing low cost compounds for use in chromium removal [58], verifying that chromium can be extracted from sludge for reuse, recovering the adsorbent, and reducing sludge toxicity [9].

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In this context, polysaccharides such as chitosan present many advantages [10,11]. Previous studies have shown that chitosan has a high capacity for sequestering many heavy metals, including chromium [12]. Moreover, chitosan is obtained by deacetylation of chitin, the main component of seafood shells, and can be obtained easily as the byproduct of fisheries. Eventually, the shells themselves can be used for chromium removal [13–15], validating the use of industrial waste for applications related to wastewater treatment, and conferring a double advantage in terms of environmental preservation. Recent studies by Aydin and Aksoy [16] and by Zykas et al. [17] address the capacity of chitosan for sequestering heavy metals and the kinetics and thermodynamics of the process in greater detail.

The aims of the present study were to assess the possibility of using shrimp shells rather than pure chitosan for chromium removal; to investigate the mechanisms involved in the removal process; and to verify that chromium can be recovered from the sludge produced during wastewater treatment.

2. Materials and methods

Initial experiments were performed using two formulations of synthetic wastewater, termed SW1 and SW2, that were prepared by adding chromium sulphate to deionized water. The concentration of Cr(III) was 4.3 g l^{-1} for SW1 and 6.7 g l^{-1} for SW2. Additional experiments were performed using real wastewater, termed RW, which had the same concentration of chromium as SW1 (i.e. 4.3 g l^{-1}). RW was taken from exhausted baths produced by a small tannery located in the province of Naples, Italy.

Analysis of chromium solubility in deionized water (DIW) was also performed. Sixteen samples of DIW containing 32 g l^{-1} of chromium sulphate were prepared, and the pH of the samples was adjusted using concentrated sulphuric acid and/or sodium hydroxide to obtain pH values ranging from 2 to 12. For each sample, residual Cr(III) was measured after filtration using paper filters with 52-µm diameter pores.

SW1 and SW2 were treated using chitosan purchased from A.C.E.F. s.p.a. (Italy). The chitosan was 92.20% deacetylated and had an ash content of 0.56%. Chitosan was added to 100 ml glass reactors containing 50 ml of SW1 or SW2 to achieve final chitosan concentrations of 2, 6, 10, 14, 18, 22, 26, and 30 mg l^{-1}, and each solution was mixed gently with a magnetic stirrer. Samples (3 ml) were removed from each mixture at timepoints that ranged from 2 to 24 h. Each sample was filtered using paper filters with 52-µm diameter pores, and the residual chromium content was analyzed.

The first experiments on RW used chitosan, and subsequent experiments used ground shrimp shells. Both chitosan and shrimp shells were added to a final concentration of 30 mg l^{-1}. Before use, the shells were washed with tap water, dried in the open air for 24 h, ground, and sieved. The experimental protocol for RW treatment was the same as that for SW1 and SW2 treatment.

The batches of sludge resulting from chitosan treatment of SW1, SW2, and RW were combined, homogenized with a stirrer, and stored at 4 °C for chromium recovery tests. Samples of sludge (20 ml) were digested using a microwave oven (Milestone, U.S.A.), and the chromium content was determined. Three additional samples of sludge (20 ml each) were diluted to 250 ml with DIW and acidified to pH 2, 4, or 5 to separate the chromium from the chitosan. After acidification, samples were filtered using a paper filter with 52-µm diameter pores, digested, and the chromium content of the material on the filter was determined. The chromium concentration of the filtrate was also measured to perform a mass balance of the metal.

When testing the use of shrimp shells to remove chromium, COD was measured in addition to pH and chromium concentration in order to determine whether organic matter was released from the waste used for the treatment process.

All reagents other than chitosan were highly pure, and only reagent-grade water treated using a Millipore MilliQ system was used as a diluting agent. Metal analysis was performed with an atomic absorption spectrophotometer (GBC, U.S.A.) Standard procedures [18] were followed for all analytic determinations.

3. Results

Figs. 1–4 and Table 1 summarize the results from tests carried out on SW1 and SW2. These experiments tested the use of chitosan as a chemical reagent to remove

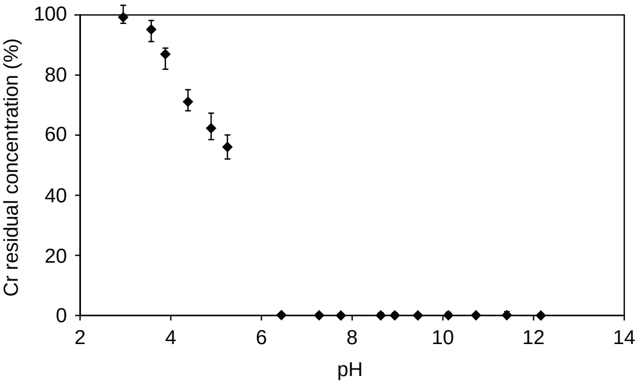

Fig. 1. Results of solubility tests.

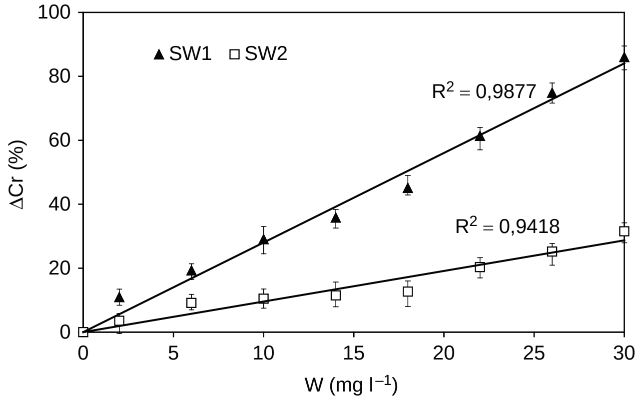

Fig. 2. Chromium removal from synthetic wastewater as a function of chitosan dose.

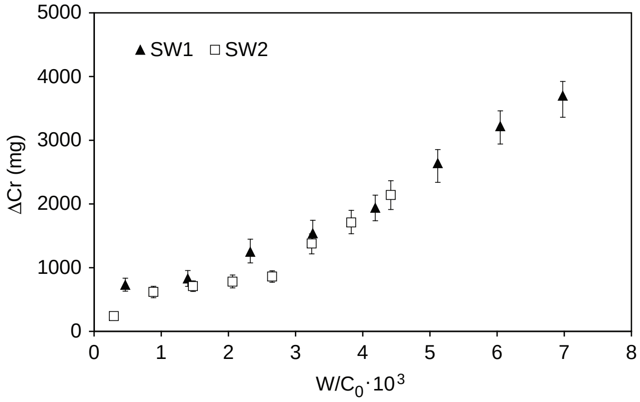

Fig. 3. Chromium removal from synthetic wastewater as a function of the ratio of chitosan dose and initial Cr(III) concentration.

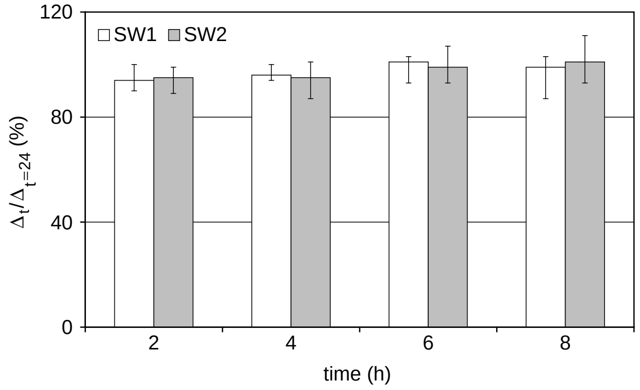

Fig. 4. Chromium removal from synthetic wastewater samples over time.

chromium and determined the main mechanism responsible for chromium removal. Taken together, the data showed that by maintaining an adequate molar

Table 1
Changes in pH after chitosan addition to synthetic wastewater

Chitosan ($\mathrm{mg\,l^{-1}}$)	pH		
	DIW	SW1	SW2
2	7.6	2.0	1.7
6	7.7	3.4	2.1
10	7.8	4.2	3.0
14	7.8	4.6	3.5
18	7.9	4.7	4.0
22	7.9	4.8	4.2
26	7.9	5.0	4.3
30	8.0	5.2	4.4

ratio between chitosan and chromium, it was possible to obtain sufficient removal efficiencies. Removal was primarily due to adsorption, which was probably mediated by the flexible structure of the polymeric groups that characterize chitosan [12]. Chromium precipitation, which is the consequence of the pH variation caused by chitosan addition, appeared to be less important for removal.

Fig. 1 shows that chromium precipitation was complete at pH > 6.0. Although the addition of chitosan to pure water increases its pH (Table 1), this increase is unlikely to occur in SW1 and SW2. At the tested dosages of chitosan, the pH varied from 7.6 to 8.0 in DIW, from 2.0 to 5.2 in SW1, and from 1.7 to 4.4 in SW2. It can therefore be inferred that chromium removal was mainly due to adsorption processes rather than to precipitation, although this remains to be confirmed by spectroscopy. In terms of removal efficiency, experiments carried out over a 24 h period with SW1 and SW2 showed that metal removal was always proportional to the amount of added chitosan (Fig. 2). Although the increase in metal removal with increased chitosan addition was more rapid for SW1 than for SW2, the trend was the same when chromium removal was plotted against the ratio of added chitosan and the initial chromium concentration (Fig. 3).

Sufficient removal efficiency (>85%) was obtained only for SW1 with 30 $\mathrm{mg\,l^{-1}}$ of chitosan. Extrapolating from the linear data in Fig. 2, it seems likely that the same efficiency could be reached for SW2 if almost three times more chitosan (88 $\mathrm{mg\,l^{-1}}$) were used. Testing samples over time showed that the process occurs quite rapidly. For example, Fig. 4 shows the results for the highest tested concentration of chitosan. For both SW1 and SW2, removal efficiency at 2 h ($\Delta_{t=2}$) was > 90% of the efficiency at 24 h ($\Delta_{t=24}$). Further, the removal efficiency was almost unchanged after 6 h ($\Delta_{t=6}$), indicating that there was almost no chromium released from the

Table 2
pH variation and chromium removal from RW treated with chitosan

Time (h)	ΔCr (%)	pH
0	0	3.7
2	95.8	5.7
4	96.0	5.7
6	97.8	5.7
8	97.7	5.8
24	97.8	5.5

metal/polysaccharide complexes. Thus, for treatment plant design, a contact time of 2 h can be used without reducing the overall efficiency of the removal process.

Experimental results obtained using RW and chitosan are summarized in Table 2 and Fig. 5. These tests aimed to confirm the results obtained with SW1 and SW2 and to investigate the possibility of recovering chromium from the sludge produced during the adsorption process. Recovery is likely to depend on the interactions between chitosan and the particular compounds (especially cations) in the wastewater.

It is important to remember that the amount of chitosan used during these tests was 30 mgl^{-1}, i.e. the maximum amount used during tests with SW1 and SW2, and that the concentration of chromium in RW was almost the same as in SW1. The results showed that the removal efficiency for real wastewater was actually better than the removal efficiency obtained for SW1. In fact, after 24 h almost 98% of the chromium was removed from RW (second column of Table 2). Due to differences in the composition of RW and SW1, addition of chitosan to RW caused a pH increase, which is quite important (third column of Table 2). Nonetheless, the pH after 24 h was still less than 6.0, and removal of chromium could still be attributed mainly to adsorption processes. The same result was confirmed by recovery tests (Fig. 5). At pH 2, the chromium recovery percentage was almost 85%, while at higher pH the recovery percentage was only 25%. Taking solubility test results into consideration makes it clear that although chromium is soluble at the pH values tested, very little was found in solutions at pH 4 and 5. Thus, the removal was not due to precipitation. Fig. 5 also emphasizes, in agreement with previous studies [11], that saturated chitosan can be regenerated and eventually reused as an adsorbent.

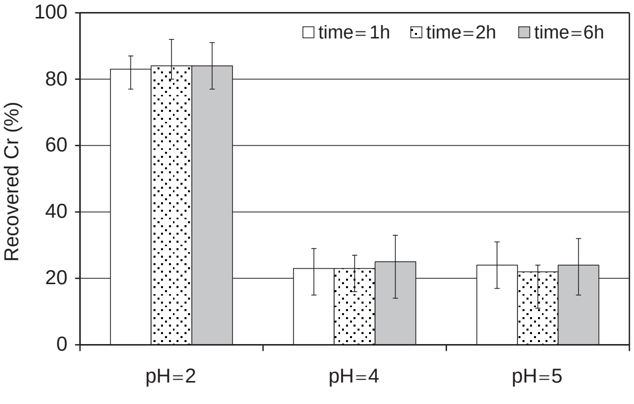

Fig. 5. Chromium recovered from sludge.

Despite the possibility that chitosan can be recovered from sludge, our interest in using this polysaccharide was based on its presence in great quantities in shrimp shells, which are a byproduct of the seafood industry. Accordingly, a third series of tests were conducted in which 30 mgl^{-1} of ground shrimp shells, rather than commercial chitosan, were added to RW. The results are summarized in Table 3.

It was immediately clear that the chromium removal efficiency obtained using shrimp shells was even higher than that using chitosan, probably due to the combination of precipitation and adsorption. The addition of shrimp shells caused a consistent pH increase: by 2 h, the pH was over 6.0, and by 24 h, the pH was 7.4. Such high pH values are conducive to chromium precipitation, as noted previously. As with chitosan, with shrimp shells it seemed that two h of reaction time were sufficient for maximal chromium removal. After two h, the removal efficiency was about 99%, a value which is comparable with those reported in the literature for other low cost materials [5-8] and which allows the treated wastewater to meet the discharge standards in the European Union and elsewhere. Although we did not test this, it is possible that a lower concentration of ground shells would be enough to obtain a sufficient removal efficiency.

It is important to note that the addition of shrimp shells caused no increase in the COD in the treated wastewater; in fact, it contributed to the removal of COD. After treatment, the measured COD was 25% lower than the initial value, decreasing from 36,400 mgl^{-1} to 27,000 mgl^{-1}.

Table 3
pH variation and chromium removal from RW treated with ground shrimp shells

Time (h)	ΔCr (%)	pH
0	0	3.7
2	98.7	6.9
4	99.5	7.2
6	99.4	7.3
8	99.4	7.3
24	99.5	7.4

4. Conclusions

- Chromium removal from tannery wastewater using chitosan is highly efficient and is primarily due to physical adsorption of chromium by polymer groups. Chromium recovery from sludge is possible at very low pH.
- Because crustacean shells are rich in chitin (from which chitosan is derived), chromium can be removed using fishery byproducts rather than commercial chitosan. Indeed, the overall efficiency is higher using shells since chromium is precipitated in addition to adsorbed due to the high alkalinity of the shells.
- Treatment with shrimp shells rather than commercial chitosan does not lead to release of COD from seafood shells during the removal process; thus, wastewater quality does not get worse in terms of organic matter content.
- Chromium removal from wastewater occurs quite rapidly after the addition of shrimp shells, and the detention time is not higher than for other low cost adsorbents.

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References

[1] C. Fabiani, F. Ruscio, M. Spadoni and M. Pizzichini, Desalination, 108 (1996) 183–191.
[2] J.W. Patterson, Industrial Wastewater Treat. Technol., Butterworth-Heinemann, London, 1985.
[3] F.N. Kemmer, The NALCO Water Handbook, MacGraw-Hill, NewYork, 1988.
[4] D. Mohan and C.U. Pittman, J. Hazard. Mater., B137 (2006) 762–811.
[5] V.K. Gupta and I. Ali, J. Colloid Interface Sci., 271 (2004) 321–328.
[6] D. Mohan, K. Singh and V.K. Singh, J. Hazard. Mater., B135 (2006) 280–295.
[7] V. Sarin V. and K.K. Pant, Bioresource Technol., 97 (2006) 15–20.
[8] L.-H. Wang and C.-I. Lin, J. Chin. Inst. Chem. Engrs., 39 (2008) 367–373.
[9] M.C. Chuan and J.C. Liu, Water Research, 30 (1996) 932–938.
[10] S.N. Kartal and Y. Imamura, Bioresource Technol., 96 (2005) 389–392.
[11] R. Cesaro, M. Fabbricino, R. Lanzetta, A. Mancino, B. Naviglio, M. Parrilli, R. Sartorio, M. Tommaselli and G. Tortora, Water Sci. Technol., 58(3) (2008) 735–739.
[12] L. Dambies, C. Guimon, S. Yiacoumi and E. Guibal, Colloids and Surfaces A. Physicochemical and Eng. Aspects, 177 (2001) 203–214.
[13] V.W.D. Chui, K.W. Mok, C.Y. Ng, B.P. Luong and K.K. Ma, Environ. Int., 22 (1996) 463–468.
[14] Y. Sag and Y. Aktay, Process Biochemistry, 36 (2001) 1187–1197.
[15] H. Niu and B. Volesky, Hydrometallurgy, 84 (2006) 28–36.
[16] Y.A. Aydin and N.D. Aksoy, Chem. Eng. J., 151 (2009) 188–194.
[17] G.Z. Kyzas, M. Kostoglou and N.K. Lazaridis, Chem. Engi. J., 152 (2009) 440–448.
[18] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, APHA, Washington D.C. 1998.