Chemical and Biological Methods as Combined Techniques for Chromium Removal from Tanning Wastewater[#]

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I N EGYPT, the tannery wastewater is discharged directly to the main domestic sewage pipeline which adds difficulties to the sewer system and to the wastewater treatment plants. Chromium has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. However, only 60% of the total chromium salt reacts with the hides. In the other word, about 40% of the chromium amount remains in the solid and liquid wastes. Therefore, the removal and reuse of the chromium content of these wastewaters is necessary for environmental protection and economic reasons. In this study, the recovery of chromium (III) was carried out by using precipitation process. To this purpose, two common precipitating agents lime and cement dust were used. The effects of precipitating agent concentration, settling rate and supernatant volume were studied in batch experiments. Results showed that the maximum chromium (III) recovery (98%) was achieved using 2g/100ml of lime and 2hr settling rate. The supernatant was further analyzed for bioremoval of soluble chromium (VI) using actinomycetes. The results showed that isolate 65S is the most efficient isolate where nearly 97% of chromium (VI) was removed over 4hrs period. This paper surveys the development of technologies that have rendered the tanning process eco-sustainable, where the combination between the chemical precipitation and the biological removal of chromium from tanning wastewater make it meet the environment safely.

Keywords: Tannery wastewater, Cr(III) precipitation, Cr(VI) bioremoval. Actinomycetes.

The tanning industry forms the backbone of the Egyptian leather industry. The total numbers of tanneries in Egypt are more than 300, of which more than 85% adopt the chromium tanning process (Ibrahim and Shalaby, 1991) because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. Tannery effluent containing chromium is one of the most

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recognized problems in leather industry. Tanning process using chromium compounds is the most common methods for processing of hides (Sreeram and Ramasami, 2003). In this process about 60% - 70% of chromium reacts with the hides. In other words, about 30%- 40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions). The wastewater of tanning process is usually discharged, without proper treatment, into the sewerage system causing serious environmental impact. In nature, chromium occurs in two major states {Cr(VI) and Cr(III)}. Even when the tanning wastewater has chromium only in trivalent form, since the tanning process does not generate chromium (VI), some countries fixed regulatory limits for the two species. This criterion appears from the assumption that the oxidation would be produced during storage and sometimes through the tanning process. Although chromium(III) oxidation to chromium(VI) occurs under specific environmental conditions (Eary and Rai, 1987), special attention is devoted to this transformation because chromium(VI) causes adverse effects for the human health (Committee on Biologic Effects of Atmospheric Pollutants, 1974) where Cr(VI) induced acute and chronic toxicity, neurotoxicity, dermatotoxicity, genotoxicity, carcinogenicity, immunotoxicity, and general environmental toxicity (Bagchi et al., 2002) and has been shown to be mutagenic in a number of bacterial systems (Nishioka, 1975; Petrilli and DeFlora, 1977). Although Cr(III) has relatively low toxicity (Palmer and Wittbrodt, 1991), when soluble Cr(III) is added to soil, manganese oxides present in the soil may cause oxidation to Cr(VI) (Bartlett and James, 1979). When not oxidized to Cr(VI) form, Cr(III) may remain immobilized in the soil.

Due to the harmful effect of chromium on human and living organisms, in addition to the cost of the chromium metal it is suggested to be recovered from the tanning wastewater (Fabiani et al., 1997; Kocaoba and Akin, 2002). There are several methods have been used for removing of chromium from the tanning wastewater as Cr(III). These methods are chemical precipitation, reverse osmosis membrane processes, and adsorption (Patterson, 1985; Ludvik, 2000). Of these, chemical precipitation is the common way for this purpose. Substances used habitually to promote the precipitation are: calcium hydroxide, sodium hydroxide, magnesium oxide or calcium magnesium carbonate. Many factors affect the process of chemical precipitation including the type of precipitation agent, pH, velocity of precipitation, sludge volume, time of mixing and complexing agents (Tsugita, and Ellis, 1981; Kocaoba, and Akin, 2002). On the other hand, advanced treatment techniques, such as reverse osmosis, ion exchange, membrane filtration, and electro dialysis are effective for removing Cr(VI), but they are expensive and generate concentrated wastes that require subsequent treatment and disposal (Komori et al., 1990). Biological removal may provide a suitable means for Cr(VI) treatment from wastewater (Lovley and Coates, 1997; Rittmann et al., 2004). Various fungal and bacterial species were reported for chromium bioremoval. However, there is no systematic study on chromate tolerance, toxicity/resistance or reduction by mycelium forming actinomycetes except few sporadic reports (Basu and Paul, 1999). Although actinomycetes constitute a significant component of the microbial population in most environments, their metabolic diversity and genomic characteristics indicate them as well suited agents for bioremoval of metal and organic compounds (Polti et al., 2007). This study aims to design a laboratory scale system to remove chromium(III) from tannery wastewater by chemical precipitation method using low cost chemicals and some by products of other industries and to study the efficiency of chromium resistant actinomycetes isolates for the bioremoval of hexavalent chromium from pretreated tanning wastewater.

Material and Methods

1. Wastewater samples were collected from selected tanneries in old Cairo after the chromium tanning stage in a composite form

The following measurements were carried out:

a) Chemical Oxygen Demand (COD)

COD concentrations were determined calorimetrically according to the method described in APHA (1998).

b) Chromium concentration

It was determined calorimetrically (l_{540}) with a spectrophotometer using the diphenylcarbazide detection method according to Bartlett and James (1991). Diphenyl carbazide solution was prepared (0.25% w/v in 50% acetone). 15 ml each of the sample solutions, containing various concentrations of Cr(VI) were pipette out into 25ml standard flasks. To this 2ml of 3M H_2SO_4 was added followed by 1 ml of diphenyl carbazide and the total volume was made up to 25 ml using distilled water such that the final concentrations were in the range of 10 to 100 mg. The intensity of the colour complex formed was measured using spectrophotometer (CECIL, CE 393, Series 2). The absorbance was measured against a reagent blank at 540-nm wavelength.

c) Turbidity

Determination of turbidity was carried out by using Digital Nephlo meter (Monitok Model 21). Ready made standards were used for calibration. Turbidity was measured as Nephlometric Turbidity Unites (NTU).

d) Determination of pH

The pH of samples was measured by digital pH meter (Toledo, MB 125. Switzerland).

2. Jar test procedure

Thirteen glass jars of 250ml volume were filled with 100ml tannery wastewater. Lime and cement dust were added with different concentrations from 0.5g to 3g per 100ml. The stirring continued for 4 min with rapid mixing of 100 rpm, followed by slow mixing for 5 min at 40 rpm. Jars were

allowed to settle for 30 min extended before taking the first samples from the supernatant for analysis then the rest of samples were taken at intervals of 30 min for 3 hr.

3. Hexavalent chromium removal by chromium resistant actinomycetes from pretreated tannery effluent

The actinomycetes isolates [11S, 65S, 46S, 79S and 46re] are chromate resistant strains previously isolated from various habitats with different background of heavy metals contamination and were able to grew in presence of 2500 mg/l of Cr(VI). The inocula of the tested strains were prepared by harvesting an overnight culture, grown in peptone water broth by centrifugation (6000g for 5min) and resuspended the pellets in sterile phosphate buffer. The actual cell density was counted as cfu/ml, 3 days after inoculating appropriate dilutions onto starch casein agar plates. Flasks contain pretreated tannery effluent were inoculated with the chromate resistant actinomycetes isolates in a cell density (18 x 10⁴ cfu/ml). The culture were incubated at 28°C with shaking at 100rpm. Chromate removal by the actinomycetes strains was monitored at different time intervals by estimating the residual Cr(VI) in the culture supernatant fluid by diphenylcarbazide detection method and COD values were also determined.

Results and Discussion

1. Effect of precipitating agents on pH of the wastewater

Different concentrations of the two precipitating agents (lime and cement dust) were added to 100ml of tannery effluent in glass jars and pH values were determined. The solution pH is an important factor in determining the physical and chemical properties of the water sample, and it can be affected by the precipitating agents. Figure 1 shows that an increase in the precipitating agent's dose is associated with increase in a solution pH. The initial pH of the sample was 3.1. After the addition of lime at a concentration of 1g/100ml, the pH increased to 5. The maximum rate of pH increasing occurs where the concentration of lime is in the range of 2-3 g/100ml, which gives a final pH values of 7.7 to 8.2, which was close to pH 8 the optimum value for Cr(III) precipitation (Patterson and Minear, 1975). In the case of cement dust, there was a little increase in pH value. After addition of 2g/100ml of cement dust, pH increased to 3.5. The wastewater tends to be acidic, and caustic or chemical addition is necessary in order to compensate the pH drop due to chromium precipitation. The presence of lime maintaining a conductive pH for the formation of Cr(OH)3 precipitate, it might also have had some coagulating effect. The pH increase indicates that coagulation of tannery wastewater could offer a possibility for treated wastewaters which may have a neutral or higher pH value. Chemical precipitation may benefit tanneries where the pH correction of acidic stream is required in order to meet discharge requirements (pH 6-9).

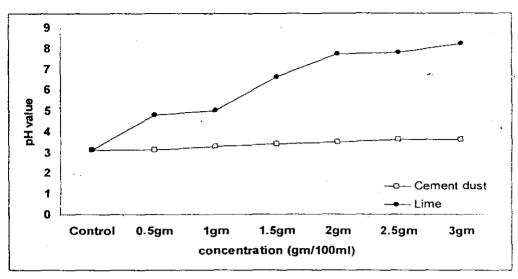


Fig. 1. Effect of precipitating agent's dose on pH of the tannery wastewater.

2. Effect of precipitating agents on COD of tannery wastewater

The effects of the precipitating agents on COD removal depend on pH value and this is shown in Fig. 2. It can be seen that COD removal is most effective (45-70 %) at a concentration various from 1.5 to 3 g/100ml of lime when the pH range was between 6.6 and 8.2, but optimally (66-70%) at concentration from 2 to 3 g/100ml. Previous reports have shown that, the rate of COD removal decreased if the pH was lower than 5.0 or higher than 8.5 (Song et al. 2003). On the other hand, cement dust additions has a little effect on COD removal it brought COD reductions by 38% at 0.5 g/100ml but when the concentration increased, the COD value increased until reach 4385 mg/l higher than the value of raw wastewater (3538 mg/l). This could be explained by the composition of the cement dust 69.5 % calcium, 12.5 % magnesium, 0.513 % ferric, 0.0313 % manganese and lime 25.08% (Rashed, 2008) which may be responsible for the COD of wastewater. Lime has a broader optimum pH range compared to cement dust. At a high pH lime addition resulted in a larger reduction of COD compared with cement dust.

3. Effect of precipitating agents on Cr(III) removal

The relationship between Fig. 1. and Fig. 3. (A,B) shows that precipitating agents dose, settling time and pH are predominant factors affecting the removal of chromium. The highest Cr(III) removal efficiency (98-99%) observed with lime treatment was attributed to the favorable pH (7.7–8.2), while 95.5-97% at pH 4.8-6.6. Settling rate was high until reach 120min but after that there was no noticeable difference. Cement dust has a different behavior, the chromium removal was very low ranged from 1.5 to 2.6% at pH 3.1-3.6 and settling time has no affect on chromium removal. This could be partly explained by the occurrence of competition between protons and metal ions under acid conditions (Sutherland, 1989). It was recommended that coagulation should be operated at an alkaline condition to achieve maximum chromium removal (Bailey and Tunick, 1982).

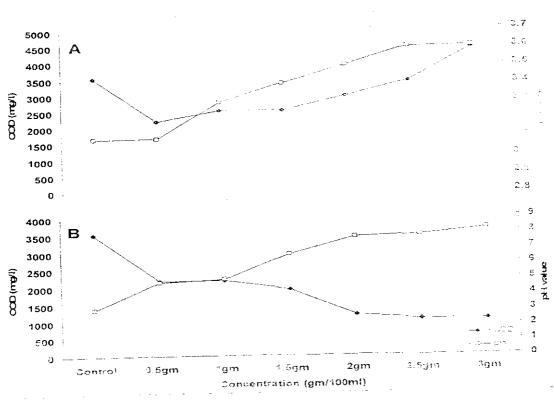


Fig. 2. Effect of precipitating agents dose and pH on COD of the tannery wastewater.
(A) Cement dust; (B) Lime.

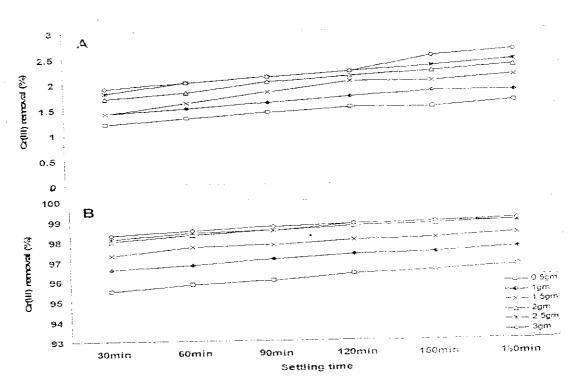


Fig. 3. Effect of precipitating agents dose and settling time on Criff() removal from tannery wastewater. (A) Cement dust; (B) Lime.

4. Cr (VI) bioremoval and COD reduction using actinomycetes

Many microorganisms are known to remove Cr(VI) from wastewaters. These microorganisms have developed a variety of mechanisms to remove Cr(VI), such adsorption to cell surfaces, transport into the cell and intra-cellular accumulation (Badar et al., 2000). It has been suggested that accumulated Cr(VI) may act as a terminal electron acceptor and reduced to Cr(III) then binds to cell wall. Many belonging to the genera Pseudomonas, Acromonas, Enterobacter, Ecoli, Bacillus and streptomyces have been reported to reduce Cr(VI) to Cr(III) Bopp and Ehrlish, 1988; Ganguli and Tripathi, 2002). The chromate resistant actinomycetes strains used during present study showed high level of chromate Explerant and accumulated substantial amount of Cr(VI) and reducing a high amount of COD from tanning wastewater. Figure 4 shows that the initial conc. of Ir(VI) was 364 mg/l. After adding the actinomycetes strains, there were a gradual decrease in Cr(VI) by the time. After 2hr of the contact between the solates and wastewater, all isolates removed from (52-57%) of Cr(VI) except 46S) removes only 33%. Control samples (without inoculated isolates) showed only 19% of Cr(VI). Then after 4hr the chromium removal began to increase 46S) removed 56% and (46re, 11S, 79S) from 70 to 73% and (65S) was the most efficient isolate removed about 90% of Cr(VI), while only 50% were removed control in control samples. Cr(VI) depletion in control may be due to spontaneous reduction or due to adhesion on the flask glass surface. Chromium concentration decreases until reach nil after 96hr in all isolates except (46S). COD reduction by chromate resistant actinomycetes strains was shown in Fig. 5. COD can be reduced by (46S, 79S, 11S) from 1.5 to 8.5% while (46re) about 28% and (65S) 30% and these results showed that there are a relationship Detween the ability of isolates for removing Cr(VI) and COD reduction in *astewater. Thus isolate (65S) can be exploited for bioremediation purposes.

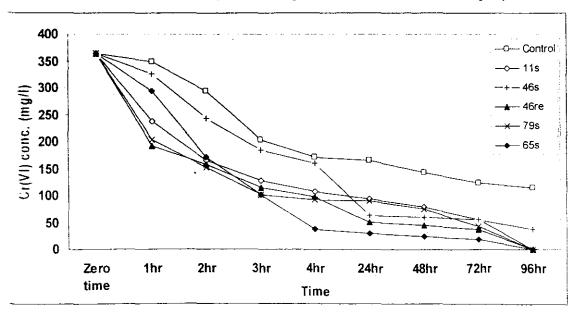


Fig. 4. Cr(VI) bioremoval from pretreated tanning wastewater using actinomycetes.

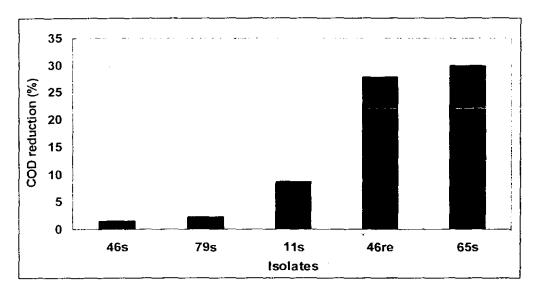


Fig 5. COD reduction from pretreated tanning wastewater using actinomycetes after 4hr incubation.

5. The efficiency of the combined technique in tannery wastewater treatment

Chemical-biological treatment of wastewater holds the promise of being more economical than either chemical or biological treatment, alone (Scott and Ollis, 1995). Table I showed the efficiency of the combined technique in the present study including chemical precipitation for Cr(III) using lime and biological removal of Cr(VI) using actinomycetes from tanning wastewater, where it improved the wastewater characteristics and removed 99.5% of total chromium, thus it could be meet the regulations for environment safety. The overall decrease in effluent toxicity following the chemical precipitation suggested not effective removal of toxic components from tannery wastewater, however, the policy of submitting wastewater to biological treatment before its release in receiving water bodies is necessary to reduce toxicity for protecting the aquatic environment (Lofrano et al., 2006).

TABLE 1. The efficiency of the combined technique in tannery wastewater treatment.

Parameter	Raw wastewater	After the combined treatment	The efficiency (%)	Max. limit of criteria and specifications (mg/l-unless otherwise indicated
pН	3.1	6.8 - 7	100%	6 - 9
Color	Dark green	Free of coloring materials	100%	Free of coloring materials
COD (mg/l)	3538	813	77%	100
Turbidity (NTU)	83.5	16	81%	50
Cr (VI) (mg/l)	364	10	97.5%	0.05
Cr (Total) (mg/l)	3250	15	99.5%	

Max limit of criteria according to Annex I of the Egyptian Law 4/94: Waste limits

Conclusion

It is concluded from our results that, the lime is a good precipitating agent for removal and recovery of chromium from tanning wastewater. The optimum pH for the precipitating chromium from tannery wastewater is 7.7-8.2 with a lime concentration (2g/100ml) and the effective settling rate was 120min. It is also concluded that the bioremoval of Cr(VI) using actinomycetes is a suitable mean for reducing the tannery wastewater toxicity. The combination between the chemical precipitation and the biological removal of chromium from tanning wastewater make it meet the environment safely.

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ازالة الكروم من مياه صرف مدابغ الجلود باستخدام تقنيات بيوكيميانية

هشام محمد عبد الله ،أنجى مجدى كمال ، عمرو حسن محمد و أحمد دويدار البسيوني الله المركز القومى النبات - كلية العلوم - جامعة قناة السويس - الإسماعيلية و المركز القومى لبحوت الإسكان والبناء - الجيزة - مصر.

أصبحت مياه صرف مدابغ الجلود وخاصة المياه الناتجة من مرحلة الدباغة بالكروم من مصادر التلوث البيني في مصر حيث أنها تهدد شبكات الصرف الصحى بالتأكل كما انها تسبب الكثير من الأضرار للبيئة سواء للتربة أو المياه الجوفيةً و ذلك نتيجه فقدان من ٢٠ إلى ٤٠ ٪ من أملاح الكروم الذي يظل غير متفاعل مع الجلد و يصرف مباشرة بصورته الحامضية الى مياه الصرف و لعدم فعالية الطرق الفيزيوكيميانية لتتقية المخلفات السائلة للمدابغ لوجود ملح الكروم في صورتين مختلفتين (الكروم الثلاثي و السداسي) و ارتفاع تكلفتها فقد اتجهت الدراسات إلى استخدام الطرق البيوكميانية كبديل فعال وأكثر أمنأ على البينة ومن ثم يهدف هذا البحث إلى : إستخدام نظام معملي لدراسة معدل استخلاص الكروم الثَّلاثي من مياه صرف المدابغ بواسطة طرق الترسيب بمواد كيميانية قليله التكلفه (الجير) و بعض مخلفات الصناعات الأخرى (تراب الأسمنت) و اختبار قدرة الاكتينوميسيتات المقاومه لملح الكروم السداسى و المعزولة من بينات مختلفة على استخلاص الكروم السداسي من مياه صرف المدابغ كمعالجه بيولوجيه تلي مرحله المعالجة الكيميانية. و قد أشارت الدراسه إلى أن أعلى نسبة لإستخلاص الكروم الثلاثي من مياه صرف المدابغ (٩٨٪) تحققت عند أضافة (٢جم/١٠٠مل) من الجير بعد ساعتين من الترسيب. أما بالنسبه إلى المعالجة البيولوجية للكروم السداسي و ذلك بحقن عزلات من الأكتينوميسيتات في مياه الصرف بعد عملية الترسيب فقد تم التخلص من حوالي (٩٧٪) في خلال ٤ ساعات. إذا نستخلص من هذه الدراسه أن المعالجة الكيميائية مع المعالجة البيولوجية كتقنية مشتركة في تتقية مياه صرف مدابغ الجلود تعتبر طريقة مثلى للتخلص من ملح الكروم والأضرار الجسيمة التي يسببها للبينة.