

Wastewater Effluent - A Case Study- Part-I

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ABSTRACT

The chromium tannery effluent wastewaters are characterized by high salt and high chromium content. In addition, the organic solids and the organic colloids are highly concentrated.

In the present case-study a medium-size tanning workshop, namely "El-Radio", Cairo-Egypt, was selected for investigation. The collected final wastewater effluent is discharged directly into the domestic sewer-network without any treatment.

The aim of the present work is to apply physico-chemical treatment results which was used previously in phase one in treating the final tannery effluent to chromium tannery wastewater effluent, to evaluate the validity of this procedure in reducing the pollution loads as a pretreatment step prior to the recovery of chromium by using membrane separation technique.

Coarse filtration as pretreatment was carried out, then followed by coagulation by using organic polymers. Three kinds of polymers (nonionic, anionic and cationic) were used.

The pretreatment technique achieved low removal efficiencies in SS, COD, and Cr. The average removal efficiencies for SS, COD and Cr are 13%, 14% and 15% respectively.

The chemical treatment by using 2.5 mg/l. nonionic polymer proved removal of pollution load to a great extent. The average removal efficiencies for SS, COD and Cr are 76%, 60% and 66% respectively.

The obtained results has been discussed evaluated and compared with the maximum national limits given by the Egyptian Environmental Law (Decree No. 44/2000) for the discharge of industrial wastewater into domestic sewerage network.

KEYWORDS:

Chromium effluent, treatment, coagulation, polymer

INTRODUCTION

The leather industry includes several processes. Chromium tanning process is one of these processes which resulted toxic wastewater effluent.

Chromium occurs in liquid wastes in two forms, trivalent (Cr III) and hexavalent (Cr VI). Hexavalent chromium is known to be a carcinogenic substance, while trivalent chromium is simply toxic. Hexavalent chromium is responsible for lung cancer^(1,2,3). The whole population dies at 1 ppm Cr⁽⁴⁾. Chromium also affects adversely air and ground quality^(5,6).

For pollution control, the effluent containing chromium must be segregated and should not be allowed to mix with other liquid wastes. This keeps the volume of the waste low. The streams can, however, be mixed after chromium has been removed.

Egyptian tanneries face now a variety of problems. One of the main problems facing the leather industry is the chromium salts lost annually in the disposed final effluent creating money losses as well as environmental degradation due to the disposal of chromium ions.

In the present case-study a medium-size tanning workshop, namely "El-Radio" in Cairo-Egypt, was selected for investigation. The collected wastewater effluent resulted from the different processes is discharged directly into the domestic sewer-network without any treatment.

Previously bench scale experiments for treatment of final effluent streams of El-Radio tannery was carried out⁽⁷⁾ where nonionic polymer of 2.5 mg/l reduce the high pollution-load to be within the limits of the biological-treatment process, which is covered by the Egyptian Government

The aim of this paper is to apply physico-chemical treatment technique used previously⁽⁷⁾ in treating the final tannery effluent to chromium tannery wastewater effluent, to evaluate the validity of this procedure in reducing the pollution loads as a pretreatment step prior to the recovery of chromium by using membrane separation technique.

PROBLEM DESCRIPTION

In tanning operation in El-Radio tannery, the salted hide is loaded in rotary drum, where 7-12 kg of tertiary chromium powder salt (25% Cr₂O₃) is used per 100 kg of hide. Basifying agent (0.5-2%) is added and drum rotation is continued for 6-8 hours. The total amount of solution in the drum during tanning usually 1.5 times the weight of hide, the chrome solution is added gradually to achieve high efficiency for hide adsorption.

A significant amount of chromium is consumed in the tanning of leather (60-80%). The liquor from the chrome tanning bath is discarded periodically as a drag out solution once its efficiency drops below a certain level.

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The chromium available in the wastewater often creates a disposal problem.

WASTEWATER CHARACTERIZATION

Six grab samples were collected from effluent of chrome tanning wastewater for El-Radio Tannery (Two grab samples of sheep-hide tanning and four grab samples of cow-hide tanning) to investigate the characterization of the chromium wastewater.

Samples collection, preservation, and analysis were carried out according to the described standard methods given by the APHA-AWWA-WPC, 1992⁽⁸⁾.

The compiled analytical results of the 6 grab samples are presented in table (1).

The chromium effluents are characterized by high salt and high chromium contents dissolved into weakly to moderately acidic medium. In addition, the organic-solids and organic-colloids are highly concentrated too, and could be estimated in the range of ± 19000 mg/l. In brief, the chrome effluent is characterized with high pollution loads from organic and inorganic species.

BENCH SCALE EXPERIMENTAL PROCEDURE

Two grab samples of wastewater chrome effluents were collected in order to cover the necessary sampling program, which include filtration and coagulation experiments. The original samples were analyzed before and after filtration and coagulation experiments in order to examine the removal efficiency of suspended solids, COD, and chromium ion.

For each experiment, a sample volume of 10 liters was filtered on a poly acrylic disc under vacuum. This step removed both solids and floating materials (fats & greases) of particle-diameter larger than 100 micron.

The Jar-test experiments were carried out at different operating conditions, and by using organic coagulants. Commercial available polymers (nonionic, anionic and cationic) were used as organic coagulants.

The organic coagulants were used in the following doses; 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 mg/l.

The samples were stirred vigorously to obtain a homogeneous medium, then a volume of 800 ml portion was taken in each of the 6 jar-test containers, and stirred at the maximum speed (120 rpm) during the addition of coagulant doses. All following results were corrected to the 1000-ml volume, normalized for sample density, and expressed in mg/l (= ppm wt/volume). After dosing, the stirring-speed was reduced to 100 rpm for 10 minutes, and then reduced again to 20 rpm for twenty minutes. Finally, the solution left to settle for 30 minutes without stirring. The sludge-volume was recorded by means of a graduated Imhof-cone for the nearest 0.1 ml, then drained, filtered, dried and weighted.

RESULTS AND DISCUSSION OF TREATMENT EXPERIMENTS

The experimental results of coarse filtration and chemical treatment for El-Radio by using organic coagulants are given in Tables 2,3 .

Table 4 summarizes the removal efficiencies after coarse filtration and the optimum doses of the used coagulants, as well as their respective removal efficiencies of SS, COD and chromium ion for both tanneries.

From coarse filtration the average removal efficiencies are (SS = 13%, COD= 14%, Cr= 15%).

From coagulation treatment, the highest mean recorded removal efficiencies (SS = 76%, COD= 60%, Cr=66 %) gained by the nonionic-polymer with 2.5 mg/l dose. The second in order was achieved by the cationic-polymer (SS = 48%, COD= 44%, Cr=38%) with a dose of 2.0 mg/l. The third in order was achieved by the anionic-polymer (SS = 33%, COD= 15%, Cr=20%) with a dose of 2.5 mg/l.

The compiled results of coarse filtration and coagulation are presented in Table 5 are still higher when we compared these results with the maximum national limits given by the Egyptian Environmental Law (Decree No. 09/1989 modified to Decree No. 44/2000) for the discharge of industrial wastewater into domestic sewerage network.

CONCLUSION

The final obtained results for chromium waste effluent (SS,COD,and Cr)are still higher as presented in tables, when we compared these results with the maximum national limits given by the Egyptian Environmental Law (Decree No. 09/1989 which modified to Decree No. 44/2000) for the discharge of industrial wastewater into domestic sewerage network.

So advanced treatment by using membrane separation to recover chrome is necessary.

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**Table 1: Compiled Analytical Results of Chromium Effluents,
For El-Radio Tannery**

| ser | Parameter | Batch-A | Batch-B | Batch-C | Batch-D | Batch-E | Batch-F | Mean | Decree No. 44/2000 |
|-----|--|---------|---------|---------|---------|---------|---------|-------|-------------------------------|
| 01 | Color | Green | Green | Green | Green | Green | Green | Green | 43 |
| 02 | pH - Value | 5.0 | 3.8 | 3.5 | 4.1 | 5.0 | 5.0 | 4.6 | 6-9.5 |
| 03 | Oil & Grease, mg/l | 74 | 83 | 613 | 75 | 674 | 121 | 273 | 100 |
| 04 | BOD-5, mg/l | 48 | 62 | 79 | 12 | 23 | 46 | 45 | 600 |
| 05 | COD, mg/l | 10482 | 3617 | 9987 | 8625 | 11928 | 10139 | 9130 | 1100 |
| 06 | Suspended Solids (S S), mg/l | 945 | 712 | 1429 | 1214 | 2479 | 1637 | 1403 | 800 |
| 07 | Volatile Suspended Solids (VSS), mg/l | 1050 | 438 | 1213 | 917 | 1851 | 1179 | 1108 | --- |
| 08 | settleable Solids | 42 | 12 | 16 | 11 | 12 | 10 | 17 | 8 in 10 min. 15 in 30 min. |
| 09 | Total Dissolved Solids (TDS), mg/l | 50959 | 44541 | 44981 | 52551 | 68105 | 51316 | 52076 | |
| 10 | Total Kjeldahl Nitrogen (TKN), mg/l | 137 | 42 | 181 | 142 | 84 | 112 | 116 | 100 |
| 11 | Sodium Ion (Na), mg/l | 14358 | 12678 | 15018 | 15983 | 24139 | 15088 | 16211 | |
| 12 | Calcium ion (Ca), mg/l | 19 | 38 | 26 | 43 | 29 | 36 | 32 | |
| 13 | Total Phosphate Ion (PO ₄), mg/l | 0.6 | 0.8 | 0.4 | 0.9 | 0.6 | 0.9 | 0.7 | |
| 14 | Chromium Ion (Cr ⁶), mg/l | 587 | 251 | 1966 | 1834 | 2321 | 612 | 1262 | T.H.M <5mg/l. |
| 15 | Sulphide Ion (S), mg/l | 76 | 81 | 51 | 58 | 64 | 48 | 63 | |

Table 2 : Bench-Scale Results of SS, COD and Cr Removal Efficiency After Filtration and coagulation For Chrome Effluent- El-Radio Tannery- RUN # 1

| Initial pH value | S.S Initial influent Mg/l | S.S after filtration mg/l | S.S Removal % | COD Initial influent mg/l | COD after filtration mg/l | COD Removal % | Cr ⁶⁺ Initial influent mg/l | Cr ⁶⁺ after filtration mg/l | Cr ⁶⁺ Removal % |
|------------------|---------------------------|---------------------------|---------------|---------------------------|---------------------------|---------------|--|--|----------------------------|
| 3.83 | 12950 | 11073 | 14.00 | 7467 | 6250 | 16.30 | 1452 | 1202 | 17.20 |

ANIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 8610 | 22.24 | 6109 | 2.25 | 1152 | 4.16 |
| 1.0 | 7690 | 30.55 | 5988 | 4.19 | 1103 | 8.24 |
| 1.5 | 7003 | 36.76 | 5800 | 7.20 | 1055 | 12.23 |
| 2.0 | 6784 | 38.73 | 5699 | 8.82 | 999 | 16.89 |
| 2.5 | 6746 | 39.08 | 5618 | 10.11 | 956 | 20.49 |
| 3.0 | 7310 | 33.98 | 6010 | 3.84 | 1010 | 15.97 |

CATIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 8000 | 27.75 | 5811 | 7.02 | 1101 | 8.40 |
| 1.0 | 6520 | 41.12 | 5519 | 11.70 | 1012 | 15.81 |
| 1.5 | 6050 | 45.36 | 4998 | 20.03 | 956 | 20.47 |
| 2.0 | 5883 | 46.87 | 4510 | 27.84 | 882 | 26.62 |
| 2.5 | 5087 | 54.06 | 3875 | 38.00 | 835 | 30.52 |
| 3.0 | 6249 | 43.57 | 4239 | 32.18 | 905 | 24.71 |

NONIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 7511 | 32.17 | 5622 | 10.05 | 942 | 21.80 |
| 1.0 | 5978 | 46.01 | 5109 | 18.26 | 790 | 34.28 |
| 1.5 | 5019 | 54.67 | 4500 | 28.00 | 620 | 48.42 |
| 2.0 | 4401 | 60.25 | 3990 | 36.16 | 549 | 54.33 |
| 2.5 | 3174 | 71.33 | 3350 | 46.40 | 413 | 65.61 |
| 3.0 | 5841 | 47.25 | 3600 | 42.40 | 485 | 59.65 |

Table 3 : Bench-Scale Results of SS, COD and Cr Removal Efficiency After Filtration and coagulation For Chrome Effluent- EI-Radio Tannery-RUN # II

| Initial pH value | S.S Initial influent Mg/l | S.S after filtration mg/l | S.S Removal % | COD Initial influent mg/l | COD after filtration mg/l | COD Removal % | Cr ⁶⁺ Initial influent mg/l | Cr ⁶⁺ after filtration mg/l | Cr ⁶⁺ Removal % |
|------------------|---------------------------|---------------------------|---------------|---------------------------|---------------------------|---------------|--|--|----------------------------|
| 3.48 | 15400 | 11600 | 12.01 | 6250 | 5508 | 11.87 | 83 | 72 | 13.25 |

ANIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 10880 | 6.21 | 5250 | 4.68 | 69.1 | 4.03 |
| 1.0 | 10090 | 13.02 | 5100 | 7.41 | 65.3 | 9.31 |
| 1.5 | 9410 | 18.88 | 4800 | 12.85 | 62.2 | 13.61 |
| 2.0 | 8987 | 22.53 | 4650 | 15.56 | 59.1 | 17.92 |
| 2.5 | 8584 | 26.10 | 4461 | 19.01 | 56.8 | 20.09 |
| 3.0 | 8811 | 24.04 | 4750 | 13.76 | 63.2 | 12.22 |

CATIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 10111 | 12.84 | 4910 | 10.86 | 64.30 | 10.69 |
| 1.0 | 8812 | 24.03 | 4408 | 19.97 | 56.20 | 21.94 |
| 1.5 | 7911 | 31.80 | 3843 | 30.23 | 51.70 | 28.19 |
| 2.0 | 7212 | 37.83 | 3408 | 38.13 | 44.10 | 38.75 |
| 2.5 | 6844 | 41.00 | 2807 | 49.00 | 39.60 | 45.00 |
| 3.0 | 7561 | 34.82 | 3101 | 43.70 | 50.20 | 30.28 |

NONIONIC POLYMER

| Dose, mg/l | S.S mg/l | S.S Removal % | COD mg/l | COD Removal % | Cr ⁶⁺ mg/l | Cr ⁶⁺ Removal % |
|------------|----------|---------------|----------|---------------|-----------------------|----------------------------|
| 0.5 | 9911 | 14.56 | 4519 | 17.96 | 61.01 | 10.99 |
| 1.0 | 8998 | 22.43 | 3608 | 34.50 | 51.21 | 28.88 |
| 1.5 | 6503 | 43.94 | 2750 | 50.07 | 41.00 | 43.06 |
| 2.0 | 4655 | 59.87 | 1910 | 65.32 | 32.01 | 55.56 |
| 2.5 | 2204 | 81.00 | 1487 | 73.00 | 24.90 | 65.42 |
| 3.0 | 3051 | 73.70 | 1520 | 72.40 | 36.11 | 49.85 |

Table 4 Summary of the Bench Scale Experiments For El-Radio Tannery Chromium Wastewater Effluent.

| Coagulant & parameter | RUN #I | RUN # II | Mean |
|--|--------|----------|-------|
| Removal Efficiency after coarse filtration: | | | |
| SS, % | 14.50 | 12.01 | 13.26 |
| COD, % | 16.3 | 11.87 | 14.09 |
| Cr ⁶⁺ , % | 17.2 | 13.25 | 15.23 |
| Anionic Polymer Coagulant | | | |
| Optimum Dose, 2.5 mg/l | | | |
| SS removed, % | 39.08 | 26.10 | 32.59 |
| COD removed, % | 10.11 | 19.01 | 14.56 |
| Cr ⁶⁺ removed, % | 20.49 | 20.09 | 20.29 |
| Cationic Polymer Coagulant | | | |
| Optimum Dose, 2.0 mg/l | | | |
| SS removed, % | 54.06 | 41.00 | 47.53 |
| COD removed, % | 38.00 | 49.00 | 43.50 |
| Cr ⁶⁺ removed, % | 30.52 | 45.00 | 37.76 |
| Nonionic Polymer Coagulant | | | |
| Optimum Dose, 2.5 mg/l | | | |
| SS removed, % | 71.33 | 81.00 | 76.17 |
| COD removed, % | 46.40 | 73.00 | 59.70 |
| Cr ⁶⁺ removed, % | 65.61 | 65.42 | 65.52 |

Table 5 : Compiled Results of the Physico- Chemical Treatment.

| Parameter | Run # I | Run # II | Average | National Limits |
|-------------------|---------|----------|---------|-----------------------------|
| S S, mg/l. | | | | 800 mg/l. |
| Initial | 12950 | 11600 | 12275 | |
| After Treatment | 3147 | 2204 | 2689 | |
| COD, mg/l. | | | | 1100 mg/l. |
| Initial | 7467 | 5508 | 6488 | |
| After Treatment | 3350 | 1487 | 1633 | |
| Cr, mg/l. | | | | T.H.M <5mg/l. |
| Initial | 1425 | 72 | 762 | |
| After Treatment | 413 | 25 | 219 | |