Recovery of Chromium from Waste Tanning Liquors by Magnesium Oxide

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Abstract
This is a case study of AL-Za’afaraniya tanning factory, 15 km to the south of Baghdad, to spot light on simple chemical treatment of the discharged water to solve the environmental problems associated with its chromium content management. The treatment was extended to the recovery and reuse of chromium. Chromium was precipitated by the addition of magnesium oxide which also acts as a neutralizer for the acidic effluent. The laboratory treatment was carried out to find the optimum conditions. The wastewater samples were taken from the outline area of the tannery. Box-Wilson method was adopted to find useful relationships between the operating variables (temperature, mixing period and magnesium oxide dose) and the pH and chromium content of effluent. The experimental data were successfully fitted to second order polynomial mathematical models for the treatment. The most favorable operating conditions for the treatment were: temperature, 30 °C; mixing period, 50 min and magnesium oxide concentration, 3000 mg/L. On using the optimum conditions a mathematical model simulating the operation for the treatment was obtained as follows:

\[Cr = 6.0848 - 0.001839 X11 - 0.105334 X12 - 0.041038 X13,\]
\[pH = 10.29086 - 0.001223 X11 - 0.140043 X12 - 0.00953 X13,\]

Experimentally Cr concentration was decreased to about (0.5 mg/L) in wastewater after raising the pH value to (7.35) by adding magnesium oxide.

Keywords: Chromium recovery; Experimental design; Heavy metal pollution; Magnesium oxide; Mineral tanning liquors

1. Introduction

The legislations with regard to the discharge of industrial wastewater are being sharpened. The trend now is to consider complete or partial recirculation and recovery of water and some valuable pollutants for economical reasons and for a sustainable development, and mainly to maintain a safe environment for aquatic life and human health, [1, 2] as well. Only in very few cases can standard solutions be applied. The best solution to wastewater problems can only be found by a team work of the industrial engineer and the industrial wastewater specialist [3]. Barbootti et al., 2009, used a combination of lime and polyelectrolyte...
for the treatment of wastewater to aid the purpose of reuse and recycle [4].

Almost all tanneries are located on rivers which provide them with process water and serve as a disposal site for their effluents. Leather industry is a high consumer of water (30 to 80 m³ for 1 ton of processed raw skins) [5]. Leather industry wastewater is a heavily polluted and characterized with color, odor, high biochemical oxygen demand, BOD and suspended solids. It contains sulphide, chromium and vegetable tanning agents and phenolic synthetic tanning agents of harmful substances. Biological treatment is used efficiently for the treatment of vegetable tanning wastewater for the reduction of BOD [6].

Chrome tan liquors are characterized by acidic pH (3-6) and high chrome salt concentration [3]. Chromium compounds in wastewater have an unfavorable effect on the life and growth of aquatic organisms [5]. Hexavalent chromium is carcinogenic at very low levels and more toxic to aquatic environment [7]. Thus, it severely affects the activated sludge process and may tend to stimulate a filamentous bulky sludge [8]. Limits of total chrome discharge in effluents are in the range 0.5 - 10 mg/L directly into water bodies, and 1-50 mg/L on indirect discharges into sewage systems [9].

In his evaluation of the treatment options and the impact of chromium from tannery effluent, Bely, 2010 [10], concluded that the treatment options are either: inefficient, complicated, energy demanding, costly or applicable to a certain parts of the world due to technology or skilled man power demand. Baig et al, 2003 [11] evaluated four chemical methods for the removal of chromium from tanning process and concluded that sodium metabisulphite is effective at low pH values to ensure 100% efficiency for both trivalent and hexavalent chromium forms.

The removal of chromium from wastewater may be accomplished by precipitation using the addition of lime and caustic soda [12]. Beleza et al., 2001 [13], used acetylene production sludge for the precipitation of Cr(III) at levels of about 2500 mg/L and attained a removal efficiency of 99% with reaction time of 180 mins. The results of the method were comparable to those obtained with other precipitation methods. Hafez et al, 2002 [14] employed RO membrane removal of unreacted chromium from spent tanning effluent and reported a chromium recovery of 98.51% at 4000 mg/L initial concentration.

Presently, the precipitation of Cr³⁺ in the form of hydroxide and to raise the pH of solution up to 8.2 followed by the disposal of the resulting sludge remains the most common practice [15]. With enough anionic polyelectrolyte, the remaining Cr³⁺ in the solution was only 0.4 mg/L as opposed to 2900 mg/L in the untreated liquor [16].

Recycling spent floats directly from chrome tanning back into processing is the simplest means of reusing chrome. Spent tanning float mixed with draining water is recycled in the following run. Other recycling techniques are also applied. Common to all techniques, however, is the need to remove leather fiber and other un-dissolved impurities by filtering the recycled floats [17].

Bentonite and porclinite are shown to be capable of extraction of trivalent chromium to a concentration of (6 ppm). Activation of the clay minerals with acid was necessary to improve the efficiency of extraction in the high chromium conc. (> 5000 ppm) [18].

The aim of the present research is at establishing an appropriate treatment (recovery) method for the acidic and chromium rich effluent of the tanning unit. The Box-Wilson method was adopted in this study. In addition, the study finds a practical utilization of the locally made magnesium oxide.
2. Experimental

2.1. General materials
Magnesium oxide (99% purity) was supplied from a local factory. Soda ash was a General purpose chemical from Hopkins & Williams. Wastewater samples were taken from the chromium unit of Al-Za’afaraniya tannery. The average chromium content was in the range of 3350-3400 mg/L, and the pH values were less than 4.

2.2. Laboratory experimental units
Fig. 1 shows a schematic diagram of the experimental unit for the chemical treatment. The unit consists of the following parts:
A water Bath of (60× 40 × 16 cm) equipped with an electrical heater of (1.2 kW) was used. A fiber glass stirrer of two blades was used for mixing with the aid of an electrical motor (1.2 kW), coupled with a regulator for speed control. A cylindrical plastic tank (30 cm diameter and 40 cm height) was used as a treatment tank. For the collection of treated wastewater, a plastic conical tank with upper diameter of (50 cm) was used. The lower discharge valve was located at the bottom and a tap was placed near the uppermost part.

Fig. 1. Schematic diagram of the experimental system; 1, mechanical stirrer (fiber glass blades); 2, water bath; 3, reactor; 4, collecting tank and 5, magnesium oxide slurry tank.

2.3. Chemical analysis
The chromium concentration in the water samples were determined by atomic absorption, AA, spectrophotometry on a Pye-Unicam SP 9-01 AA spectrophotometer (Cambridge, England). The operating conditions were as specified by the manufacture. The chemical composition of the solid products was done by X-ray diffraction using a Philips P.W.- 1840 Diffractometer. The activation energy was 40 KV at 20 mA. The Cu-kα line was used (1.54 Å). For pH and dissolved oxygen determination, the universal pocket meter multi line P4, which consists of a pH combined electrode with temperature probe Sen Tix 41 and dissolved oxygen probe, Cell Ox 325 was used.

2.4. Procedure
In accordance with the design of the experiments shown in Table 1, twenty experiments were carried out with various operating conditions using real wastewater from the mineral tanning plant after screening to get rid of materials like, hair and skins pieces. Four liters of the wastewater were placed in the reactor located in the bath at the desired temperature. Magnesium oxide was added as slurry, where the calculated amount was stirred with sufficient volume of water. The final concentration of Cr was corrected for the volume of MgO slurry added. MgO slurry was added to the wastewater and the mixture was stirred for a previously specified time. The stirrer is switched off and the chromium precipitates was in the form of a compact sludge.

Following the Box-Wilson method of experimental design, [19] the operating parameters used, were in the range:
\[ T = 20 – 40 °C; \]
\[ t = 15 – 60 \text{ min.}; \]
\[ \text{MgO concentration} = 1000 – 3000 \text{ mg/L}. \]

2.5. Natural sedimentation
In this stage, the treated wastewater was clarified in the conical tank for about 5 - 7 hours and the clear liquid is decanted off. A specified volume of the clarified water was
taken and total Cr concentration is measured. The pH of this water is measured using the Sen Tix 41 type device.

3. Results and Discussion

3.1. Preliminary experiments

Prior to the present analysis, magnesium oxide was added to a wastewater sample from chromium plating factory to recover chromium values. The process comprised contacting the acidic solution containing sulfate ion and trivalent chromium ion with at least about 4 molar equivalents of MgO per 3 molar equivalents of trivalent chromium to aid acid neutralization to a pH of about 4 to from an amorphous, dense solid, grainy, easily settable precipitate. This is in agreement of the reported documents on the utilization of MgO for chromium recovery [21]. The water remaining after separation of the precipitate contains less than 0.5 mg/L chromium which is in agreement with some reported results [22].

The treatment of the chromium tanning effluent with MgO gave compact sludge that is easy for removal by decantation. This in part may be explained in accordance with Lippmann’s theory [23] where the basicity at the MgO surface that would be strong enough to precipitate many of heavy and hazardous metals encountered in wastewater streams. Besides, the metal precipitates are negatively charged, so they cement to the MgO surface to give compact sludge and denser residues than obtained with lime. Regeneration of the MgO filter precipitant by backwashing and chemical stripping with EDTA would allow for recovery of heavy metals in a concentrated form.

Table 1. The coded and real variables and the response values of the resulting solution using central composite method.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Coded variable</th>
<th>MgO Conc., X1 mg/L</th>
<th>Temp., X2 °C</th>
<th>Reaction Time, X3 min.</th>
<th>Cr ppm</th>
<th>pH</th>
<th>% Recovery of Cr</th>
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<td>24</td>
<td>25</td>
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<td>24</td>
<td>25</td>
<td>1.07</td>
<td>7.95</td>
<td>99.968</td>
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<td>7.26</td>
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<tr>
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<td>8.23</td>
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</tr>
<tr>
<td>5</td>
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<tr>
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<tr>
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<td>7.26</td>
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<tr>
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<td>8.42</td>
<td>99.980</td>
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<td>7.54</td>
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<td>2000</td>
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<td>16</td>
<td>0/0/0</td>
<td>2000</td>
<td>30</td>
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<td>1.02</td>
<td>7.54</td>
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<td>17</td>
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<td>2000</td>
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<td>2000</td>
<td>30</td>
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<td>1.02</td>
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<td>7.54</td>
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<tr>
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<td>0/0/0</td>
<td>2000</td>
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<td>38</td>
<td>1.02</td>
<td>7.54</td>
<td>99.970</td>
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</tbody>
</table>
Typical applications of granular MgO include wastewater with a pH greater than 5 and metal concentrations up to 25 mg/L and for more acidic or higher metal concentrations, treatment with magnesium hydroxide slurry or magnesium oxide powder is recommended [24].

The solid residues formed were dried and washed with ethanol and further dried and kept for identification with x-ray diffraction. The diffraction lines were compared with the ASTM standard tables. The following compounds were identified: Cr₂(SO₄)₃ at pH values less than 2.0; Cr₂(OH)₃(SO₄) at pH 3.0 – 4 and and Cr(OH)₃ at pH values above 6.5. Thus, the pH of the solution is a major parameter in determining the composition of the products formed. At pH values of 8.0 to 9.9, Cr(OH)₃ is virtually insoluble [25].

3. 2. Postulating the mathematical model

A second order polynomial equation was employed in the range of the three independent variables to yield the equations relating the chromium concentration and the pH of the resultant solution to these variables. Table 1 show the coded and real variable used in the present study together with the response which is the Cr concentration and the pH values of the treated water. The regression analysis of central composite design can be applied to the approximating model to obtain the optimum conditions for the treatment process. Using statistic software, the coefficients of the response equations (1 and 2) were determined:

$$\text{Cr} = 6.084884 - 0.001839 \, X_1 - 0.105334 \, X_2 - 0.041038 \, X_3 - 0.00005 \, X_1^2 + 0.00001 \, X_2^2 - 0.000138 \, X_3^2 - 0.000005 \, X_1X_2 + 0.001675 \, X_1X_3 + 0.00017 \, X_2X_3$$

(1)

Correlation Coefficients (R) = 0.9757

Variance Explained = 95.206%

Final Loss = (Observed – Predicted)² = 0.10862

$$\text{pH} = 10.29086 - 0.001223 \, X_1 - 0.140043 \, X_2 - 0.00953 \, X_3 + 0.00003 \, X_1^2 - 0.000001 \, X_2^2 + 0.000161 \, X_3^2 + 0.000001X_1X_2 + 0.001386 \, X_1X_3 + 0.000084 \, X_2X_3$$

(2)

Correlation Coefficients (R) = 0.9988

Variance Explained = 99.77%

Final Loss = 0.005079

To test the significance of each term in equation (1) and (2), the F- distribution test [26] was used employing the variance of each term in multivariable correlation, according to Table 1. The analysis of variance for orthogonal variables gave the results shown in Table 2. The observed and predicated response and their errors for chromium conc. Values are listed in Table 3. From Table 3:

$$\text{SEE} = \sum (Y_{obs} - Y_{pred}) = 0.1087$$

(3)

The computed F- values are compared with the critical F- values at (α) value of 0.05 (95% confidence) with (n – j-1) to give the critical F-value F_{α(1,10)} = 4.96. According to Table 2, the terms of interaction between the variables (X₁X₃, X₁X₂, X₂X₃) are insignificant. Thus, it is clear that the best form of equation (1) is:

$$\text{Cr} = 6.084884 - 0.001839 \, X_1 - 0.105334 \, X_2 - 0.041038 \, X_3 - 0.00005 \, X_1^2 + 0.00001 \, X_2^2 + 0.000138 \, X_3^2$$

(4)

Similarly the terms of interaction between the variables (X₁X₂, X₂X₃) of equation (2) were found insignificant. Thus, the best form of equation (2) is:

$$\text{pH} = 10.29086 - 0.001223 \, X_1 - 0.140043 \, X_2 - 0.00953 \, X_3 + 0.00003 \, X_1^2 - 0.000001 \, X_2^2 + 0.000161 \, X_3^2 + 0.001386 \, X_1X_3$$

(5)

3. 3. Optimization of operating variables:

Using the coded data of central composite design, the coefficients of the equations were determined by using Statistica software. The relationships of MgO addition, X₁,
temperature, $X_2$, and Mixing period, $X_3$ with chromium concentration and the pH of the resultant solution can then be represented as:

$$
Cr = 6.084884 - 0.001839 X_1 - 0.105334 X_2 - 0.041038 X_3
$$

(6)

Correlation Coefficients (R) = 0.9757

Variance Explained = 95.206%

$$
\text{pH} = 10.29086 - 0.001223 X_1 - 0.140043 X_2 - 0.00953 X_3
$$

(7)

Correlation Coefficients (R) = 0.9988

Variance Explained = 99.77%

The optimum conditions were estimated from these equations:

$X_1$ = Magnesium Oxide addition = 3000 mg/L

$X_2$ = Temperature = 30 °C

$X_3$ = Mixing period = 50 min.

For the starting Cr concentration of 2500 mg/L, the optimum MgO value refers to a molar ratio of 3:2 Mg:Cr. The optimum mixing period above is shorter than that reported earlier with the use of acetylene production sludge [13]. The remaining chromium concentration in effluent was 0.5 mg/L and the pH = 7.35 which are in accordance with the valid legislations. The remaining chromium content was comparable to those obtained with anionic polyelectrolyte [16].

3. 4. Effect of operation variables on the chromium concentration

3. 4. 1. Magnesium oxide addition

The effect of the various MgO additions on the levels of chromium concentration in the effluent at various temperatures and mixing period are shown in Figs 2 and 3. It is clear that, at a fixed mixing period of 50 min., the chromium concentration in the effluent drops to 0.5 mg/L, at magnesium oxide addition of 3000 mg/L and a temperature of 30 °C. Meanwhile, at a temperature of 30 °C, the chromium concentration in the effluent decreases rapidly when MgO addition increase up to 2000 mg/L. Beyond this, the chromium concentration decreases slowly to reach 0.5 mg/L at MgO addition of 3000 mg/L.

![Fig. 2 Effect of MgO addition on chromium concentration at fixed mixing period (50 min) at 20 °C, •, 24 °C, ◆; 30 °C, ◇; 36 °C, ▼ and 40 °C, ▼.](image)

![Fig. 3 Effect of MgO addition on chromium concentration at fixed temperature (30 °C) after mixing for 15 mins, ◆, 25 mins, ◆, 38 mins, ◇; 50 mins • and 60 mins, ▼.](image)

3. 4. 2. Temperature

The effect of temperature on the chromium concentration at different mixing period and magnesium oxide addition are shown in Figs 4 and 5. In two dimensional form, Fig. 4 shows that at a constant magnesium oxide addition (3000 mg/L), the chromium concentration decreases with increasing temperature down to a value of 0.5 mg/L at 30 °C and mixing period of 50 min. Beyond this temperature the Cr concentration increases. On the other hand, Fig. 5. shows that at constant mixing period of 50 min., chromium concentration reaches 0.5 mg/L at temperature of 30 °C and MgO addition of 3000 mg/L.
Table 2. Analysis of variance for orthogonal variables.

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<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>Computed f</th>
<th>Conclusion</th>
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Table 3. The observed and predicated response and their errors for chromium concentration values.

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% average absolute error = 0.615%.
3. 4. 3. Mixing period

The effect of mixing period on the chromium concentration in effluent at different MgO addition and temperature are shown in Figs 6. and 7., respectively. The figures indicate that the chromium concentration decreases slowly down to a value of 0.5 mg/L at 50 min. and 30 °C, and remains almost constant. Thus, it was not necessary to increase the temperature further.

3. 5. Effect of operation variables on pH value
3. 5. 1. Magnesium oxide addition

The effect of magnesium oxide addition on pH of the effluent at different temperature and mixing period are shown in Figs 8. and 9. The pH of the effluent increases slowly with increasing the addition of MgO to 3000 mg/L, the pH increased up to a value of 7.35 at 30 °C. On the other hand, at a temperature of 30 °C, the pH increases rapidly to reach a value of 7.35 with increasing the magnesium addition to 3000 mg/L at a mixing period of 50 min.
3. 5. 2. Temperature

The effect of temperature on pH at different mixing period and MgO addition are shown in Figs 10. and 11., respectively. The figures indicate that at a fixed MgO of 3000 mg/L, the pH increases rapidly with increasing the temperature. Further, there was no need to increase the temperature above 30 °C where the optimum point occurs at pH of 7.35. On the other hand, at a fixed mixing period of 50 min., the pH increases with increasing temperature.

3. 5. 3. Mixing period

The effect of mixing period on the pH of the effluent at different magnesium oxide concentration added and temperature are shown in Figs 12. and 13., respectively. The pH values increases with increasing the time at a temperature of (30 °C). Meanwhile, the pH of the effluent decreases with increasing the mixing period at fixed magnesium oxide addition.

3. 6. Large scale experiment

A 20 liter sample of wastewater was treated similarly using the optimum conditions obtained above. It was observed that 250 g of sludge can be obtained containing chromium as CrSO₄·H₂O with Cr₂O₃ content of 30.35% in addition to magnesium hydroxide as a compact material that can be separated by treating with Na₂CO₃ or H₂SO₄.

However, the present, rather simple, treatment compares well with the results of Rao [27], who reported an efficient recycling of unused chromium as well as water with electrodialysis technique using Sellemion AMV and CMV membranes and a prototype electrodialysis cell. Besides, it resulted in improved sludge properties in comparison with the system adopted by the European countries [28] which uses soda ash or some other alkali is added to promote the combination of the tanning agent with skin substance.
Fig. 11. Effect of temperature on pH of the effluent at fixed mixing period (50 min) for MgO concentrations of 1000 mg/L, •; 1432 mg/L, ◦; 2000 mg/L, ◇; 2577 mg/L, □ and 3000 mg/L, ◁.

Fig. 12. Effect of mixing period on pH of the effluent at fixed temperature (30 °C) for MgO concentrations of 1000 mg/L, •; 1432 mg/L, ◦; 2000 mg/L, ◇; 2577 mg/L, □ and 3000 mg/L, ◁.

Fig. 13. Effect of mixing period on the pH of the effluent at fixed MgO addition (3000 mg/L) at 20 °C, ◆; 24 °C, ◦; 30 °C, ◇; 36 °C, □ and 40 °C, ◁.

4. Conclusions

The efficiency of magnesium oxide to remove heavy metals is increasing when the concentration of these metals is increasing in the wastewater being under treatment. This fact is very clear when we compare the removal efficiency of magnesium oxide in electroplating and tanning wastewater. The use of MgO is beneficial as it neutralizes the acid medium, produces dense and consequently lower volume sludge. This helps in the control the cost of sludge handling in comparison with calcium hydroxide and sodium hydroxide.

References