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Investigation and Optimization of Electrochemical Deposition Approach Used for Recovery of Chromium from Tanning Wastewater

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Abstract: The removal of the chromium from spent tannery solution was carried out by electrochemical technique in order to minimize the pollution problem of tanning process activity using platinum as anodic electrode and iron, aluminum, nickel and copper as cathodic electrode. The volume of cell was 250 cm^3. A treated synthetic bath solution contains 12.87 g/L of $Cr(OH)SO_4$. The current density range was (1.5-3.5) $A.dm^{-2}$ and the temperature (25-45)°C. Three organic acids (formic acid, citric acid and acetic acid) were used as additives to improve electro deposition. The removal percent is determined by using atomic absorption spectrophotometer. The best removal of chromium is 97.11% after 4 h, the best temperature is 35°C and the best current is 3.5 $A.dm^{-2}$. The powder obtained from the deposits on the cathode was analyzed by X-ray diffractometer, differential scanning calorimetry and fourier transform infrared. They were shown that the powder was composed of Cr_2O_3 after heating. The chromium electro-deposition takes place because of the formation of active chromium-carbamid complexes. The complex compounds were expected as formate, citrate and acetate of chromium.

Key words: Chromium, tannery, electrodeposition wastewater, electrochemical cell, pollution, transform

INTRODUCTION

Tanning is one of the well-known and oldest leather processing industries in the world. It is commonly known as a polluting industry due to the wide varieties of highly toxic chemicals produced (Chowdhury *et al*., 2013). The most common effective process for hides treatment is tanning by using chromium compounds (Ram *et al*., 1997) where trivalent chromium (Cr (III)) is commonly employed as tanning agent and it is recognized as a dangerous environmental pollutant (Song *et al*., 2000).

The common wastewater treatment methods are the biological treatment and the primary treatment (coagulation method) (Song *et al*., 2004; Canizares *et al*., 2006). The biological method is not widely used because of the existence of broad-spectrum biocides utilized in the hides industry to avert fungal attack (Meneses *et al*., 2005).

Utilizing the most appropriate wastewater treatment method count on several points such as efficiency, cost and environmental capability (Costa and Olivi, 2009). The removal of chromium by using chemical processes are fairly complicated, expensive, slow and employing chemical reagents, however, the electrochemical processes are simpler, economical, quick. Moreover, the depositions in the electrochemical case can be reused again or utilized for further purposes. Therefore, electrochemical process has received increasing attention in the last years (Farmer *et al*., 1997).

A less explored alternative for the electrodeposition of chromium is the application of Cr (III) ionic liquid solutions. Ionic liquids have several characteristics that make them interesting for electrochemical applications: high thermal stability, good conductivity, recyclability (Endres and El-Abedin, 2006).

However, it is quite difficult to achieve thick deposits of trivalent chromium. The main barrier seems to be the formation of trivalent chromium hydroxo-complexes around the electrode during Cr-deposition. The electrode surface may be blocked by poorly soluble adsorbed hydroxide compounds of Cr (III). Therefore, the chromium depositing rate minimizes (Protsenko and Danilov, 2009).

Recently, the trivalent Cr-baths which include carbamide formate and such complex agents were studied. However, the influence of bath composition and electrodeposition conditions on the current density, electroplating rate and surface morphology of Cr-coatings obtained from Cr(III) bath which contains carbamide and formate has been studied insufficiently (Kuznetsov *et al*., 2001; Survilene *et al*., 2006, 2007).

MATERIALS AND METHODS

Tannery wastewater characterization: The tannery waste water which is utilized into the electrochemical treatment

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was collected from the treatment tank of a tannery that had processed leather until completely treated leather was achieved.

Total chromium concentration is determined by atomic absorption using atomic absorption spectrophotometer type (AA320N, Hanker, Hongkong) flame spectrometer and a hollow cathode lamp for chromium operating at 357.9 nm with a slit of 0.5 nm.

Chloride concentration was examined by potentiometric titration with a $AgNO_3$ 0.1 mol/L solution using a combined-silver wire indicator electrode coupled to a Minipa Model 207 pH meter/potentiometer. The pH was measured by pH meter type (pH211, Hanna, USA).

Preparation of tanning solution: Analytical grade Cr $(OH)SO_4$ (12.87 g) and (4 g) of NaCl was dissolved in 1 L deionized water to prepare the chromium solutions for all experiments. Three organic acids (formic acid, citric acid and glacial acetic acid) were added to the tanning solution as a couple and triple the amount of each acid was 1-3 mL.

Specimen preparation: Specimen (5.5*10 cm) were abraded in sequence by emery papers of the following grades (100, 200, 400, 600) under running tap water and dried with tissue paper, then immersed in ethanol for 1-2 min and dried with tissue paper.

The electrochemical cell: Batch electrochemical cell was used. The quadratic cell was divided into anode and cathode compartment. The current passed through electrodes. Titanium coated with platinum plate was used as anodic electrode. The iron, aluminum, nickel and copper were used as cathodic electrode. Shape and dimension of the anode and cathode are similar. To prevent channeling, the distances between the electrodes is 2 cm. The exposed area is 66 cm^2. The volume of the solution is 250 mL.

The electrochemical cell with its measuring instruments and power supply were arranged to achieve electrochemical precipitation. The electrochemical techniques consists of two cathodic electrodes (working electrodes) and one anodic electrode (inert) between them. The electrodes connect to the DC power supply and ammeter connected in series as shown in Fig. 1.

All the experiments were duplicated current densities (1.5, 2.5 and 3.5) $A.dm^{-2}$. The experimental was carried out at different temperature (25, 35 and 45)°C and concentration of chromium measured at 1-4 h. The volume of sample is 1 mL.

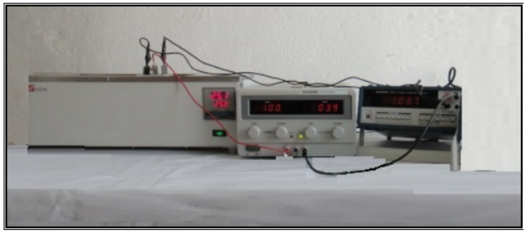

Fig. 1: The cell connection with PS and Ammeter

RESULTS AND DISCUSSION

In all tests, the percent of separation was carried out by using atomic absorption spectrometer technique. All results are the average of two tests. Furthermore, differential scanning calorimetry, X-ray diffractometer and fourier transform infrared were used to recognize the type of compound or group deposited.

Effect of temperature: Three temperatures (25, 35 and 45)°C were used for all compositions and metals. The range of temperature used is classified as moderate temperature. Chromium removal gradually increases with temperature increasing from 25-35°C. The removal percentage of chromium raises to a maximum value of 97.11% at a temperature of 35°C and then it declines at 45°C as shown in Fig. 2 while Arrhenius equation states that the reaction rate increased with increasing temperature. Langkam J. thought that the increase in the reaction rate then decrease is due to the nature of the process which it exothermic reaction (Langkam, 2011).

It was suggested that the decrease in the deposition of chromium due to the porous deposition which will dissolve in the solution at temperature equal to 45°C as shown in Fig. 2. Therefore, the optimal value of bath temperature is about 35°C (Hordienko *et al*., 2011). Note that, the increasing of the current density leads to increasing temperature, deteriorating the outward appearance of the deposits and decreasing the rate of electrodeposition.

Effect of current: Figure 3 clarify that, the maximum chromium removals were accomplished at high current values and have good agreement with Faraday law. While increasing the current will increase the flow of electrons and therefore a greater electrostatic attraction. Moreover, at higher current values the functional groups of carboxyl and hydroxyl ion became more active to achieve higher ability for deposition on the cathodic electrode, resulting in increased chromium removal (Liu *at al*., 2011).

Generally, the efficiency of current is changed randomly. The current density (2.5 $A.dm^{-2}$) gives the best

Table 1: Current efficiency of chromium removal at different temperature (25, 35 and 45)°C, time (1-4) h and current density (1.5, 2.5 and 3.5) A.d m^{-2} with addition (3 mL of acetic acid, 3 mL of formic acid and 3 g of citric acid) and using nickel as a cathode electrode

	Current density (A.cm^{-2})								
Temperature (°C)	25			35			45		
Time (h)	1.5000	2.5000	3.5000	1.5000	2.5000	3.5000	1.5000	2.5000	3.5000
1	26.170	31.327	28.544	29.608	31.938	29.262	24.514	31.913	27.998
2	25.395	31.805	28.419	29.561	33.653	31.455	23.620	31.491	27.816
3	26.526	30.907	27.342	30.115	30.953	27.708	24.061	29.708	26.327
4	25.225	25.036	21.715	28.425	25.476	21.972	22.678	23.935	20.666

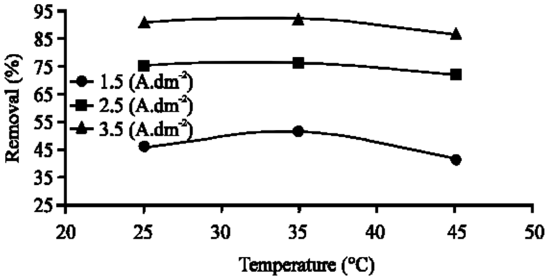

Fig. 2: The removal of chromium versus temp. at different current, 3 mL of acetic acid, 3 mL of formic acid and 3 g of citric acid and iron as a cathode

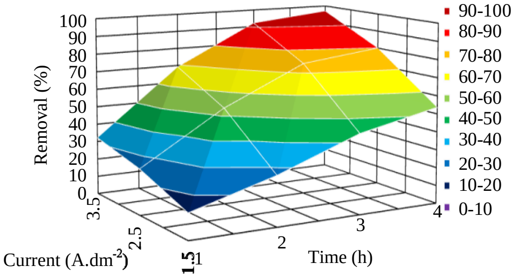

Fig. 3: The removal of chromium versus current at temp. 35°C and different time, 3 mL of acetic acid, 3 mL of formic acid and 3 g of citric acid and iron as a cathode

efficiency. At current density (3.5 A.dm^{-2}), the efficiency is reduced due to the gases liberation through the experiment. At current density (1.5 A.dm^{-2}), the efficiency is reduced due to the slow reaction which results little removal of chromium as shown in Table 1.

Effect of time: The removal percentage of chromium increases with increasing time and the maximum removal is 97.11% in 4 h for nickel as cathode electrode as shown in Fig. 3.

Figure 3 clarify the variation of chromium removal percent with the electrodeposition time. The recovery of chromium ions in the form of $Cr(OH)_3$ occurred at a higher rate because of its greater deposition capacity under optimized conditions which reached 92.08% in 3 h and the rate through the 4th h is slower and reaches 97.11%.

At current density (1.5 A.dm^{-2}), the chromium removal rate is almost linearly with time. While the removal rate of chromium decreases with time at current densities 2.5 and 3.5 A.dm^{-2}. The rate of removal in the 4th h is very small. In all experiments, the decrease of deposition could be related to the resistance of the deposition layer and sharp decrease in concentration of chromium ions in the solution.

The chromium deposition rate decreases over time due to the potential of concentration polarization where ions are reduced continuously due to the change in concentration of Cr (III) and Cr (VI) ions into the bulk and around electrode.

The Cr (III) is converted to Cr (VI) due to current flow. The rate of conversion at current density of 3.5 A.dm^{-2} is higher than the rate at current density of 2.5 and 1.5 A.dm^{-2}.

Effect of additives: In all cathodic materials used, the chromium removal was affected by the composition of deposited layer, the complex compounds formed and the chemical and physical properties of the deposition layer. The addition of three organic acids to the solution increases the chromium removal percent which related to complex compounds formed and makes deposition process continuous where the mixture used leads to stop or retard the electrodeposition as shown in Fig. 4.

The best results obtained could be related to the complex compounds which may be formed mainly (Chromium formate, Chromium citrate and Chromium acetate). Protsenko *et al*. (2011) thought that there is no explanation to this behavior and the analysis of these cases were related to the complex compound formed. The trichromium salts or complexes formation are only possible if there are two acids or hydroxyl ligand available per chromium. The weaker acids have the stronger ability of formation stronger complex compounds (Samir, 1996). The added acids are considered as weak acids. The suggested complex compounds are shown in Fig. 5.

Effect of cathode material: The recovery process of chromium from tanning wastewater has been done by utilizing platinum as an anode and (iron, nickel, copper

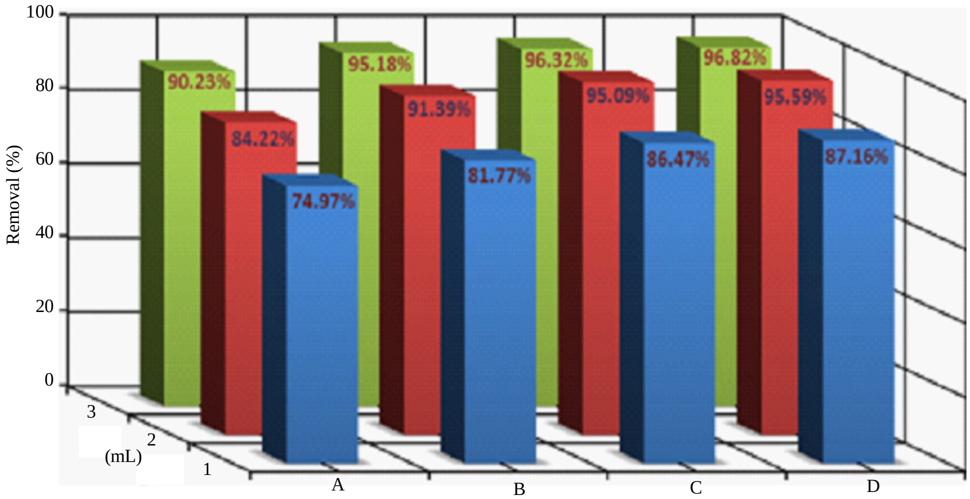

Fig. 4: The removal of chromium versus type of mixture at current density 3.5 A.dm^{-2}, temperature 35°C and iron as a cathode electrode where; A) Acetic and citric acids; B) Acetic and formic acids; C) Citric and formic acids and D) Acetic formic and citric acids

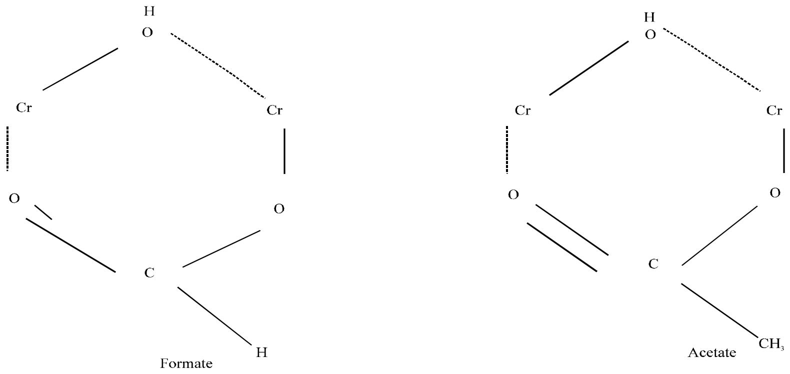

Fig. 5: The suggested complex compounds

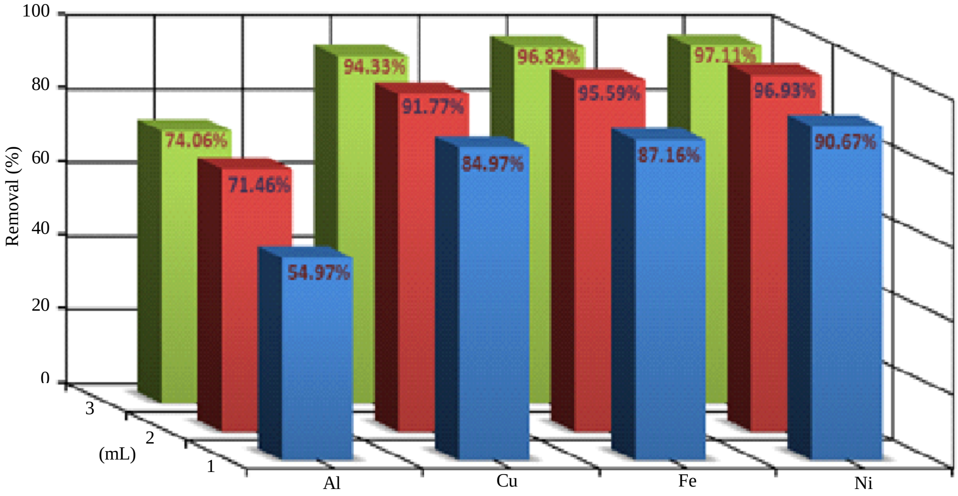

Fig. 6: The chromium removal versus cathode material at current density 3.5 A.dm^{-2} and temperature 35°C 3 mL of acetic acid, 3 mL of formic acid and 3 g of citric acid and iron as a cathode

and aluminum) as a cathode at various temperature and current density. The chromium removal rate was significantly affected by the type of anode and cathode and other electrochemical factors as shown in Fig. 6. The platinum is an inert (noble) anode which could contribute to provide a smooth current and promoted recovery of chromium.

Figure 6 shows that, the best removal (97.11%) is obtained by using nickel as a cathode in mixture containing of 3 mL glacial acetic acid, 3 mL formic acid and 3 g citric acid. In contrast, the lowest removal (74.06%) is obtained by using aluminum as a cathode in the same mixture. It was observed that there is no deposition on the surface of aluminum electrode and there is dissolution of its ions in the solution making sludge in the cell although it is a cathode.

Due to aluminum lower removal percentage obtained, there was small difference in removal percentage in changing temperature and current and have same trend as for iron electrode. However, iron is better than copper as a cathodic electrode. From the above results, the nickel has highest percent of removal which could be related to the nickel properties (smooth and shine surface which make it easy to remove the deposition). Moreover, it was observed that some reddish-brown stain on the iron and a green layer on the surface of the copper due to oxidation formation.

X-ray diffraction: The powder deposited on the cathodic electrode was analyzed using X-ray diffraction technique. The XRD pattern of the specimen not shown. Broad peaks were gained instead of sharp peaks indicate that the specimen was poorly crystalline (amorphous).

The samples must be heated to certain temperature to increase its crystallinity. Powder was tested by differential scanning calorimetry to indicate temperature limits (325°C) which could be used for crystallization of the powder as shown in Fig. 7. The expected groups that they might be existed in powder are acetate and formate. All the groups mentioned decompose at temperature of 300°C and above.

Figure 8 shows the XRD test for heated sample (crystalline). The observed positions of the diffraction lines (2θ and corresponding $d_2\theta$) for the patterns are in full agreement with the corresponding values reported for Cr_2O_3 (JCPDS, Card No. 38-1479).

Fourier transform infrared: FTIR study of the sample was accomplished to illustrate the presence of various groups and structures in the material by the important peaks and probable corresponding to the functional groups.

Figure 9 shows that, the broad peak of the sample at 3375 cm^{-1} was resulted from the overlapping of O-H stretching. The second peak at 1475 cm^{-1} is indicating the presence of C-H bending and peak at 1610 cm^{-1} is arising from C = O carboxylates salt. However, the two band peaks at 1075 cm^{-1} represent existence of the vibration peaks of C-O bond. The presence of O-H, C = O, C-H and

Fig. 7: The DSC test for sample

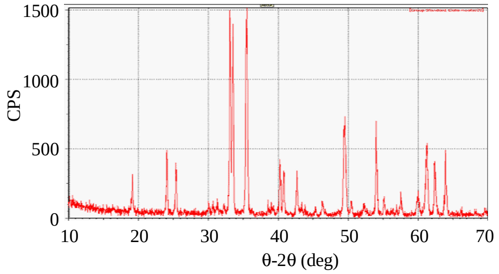

Fig. 8: XRD test for heated sample (crystalline)

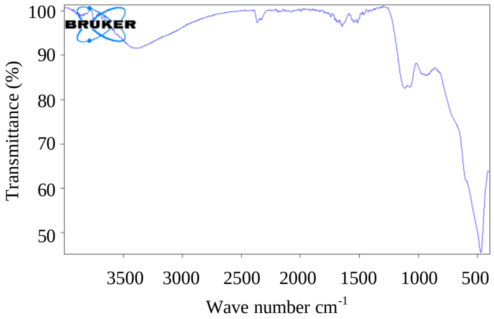

Fig. 9: FTIR spectra of (3 mL of acetic acid, 3 mL of formic acid and 3 g of citric acid) and iron as a cathode electrode

C-O leads to the expectation that the acetate format and citrate is formed in the deposition layers as a complex compound.

CONCLUSION

According to the results obtained, several points may be drawn and can be summarized as follows:

- the electrodeposition of chromium increases as current density increases
- The greatest efficiency of chromium removal is (97.11 %) when the cathode material is nickel
- Chromium removal efficiency is highly depended on the type and amount of additives
- The chromium electrodeposition occurs due to the formation of active chromium-carbamide complexes

REFERENCES

Canizares, P., F. Martinez, C. Jimenez, J. Lobato and M.A. Rodrigo, 2006. Comparison of the aluminum speciation in chemical and electrochemical dosing processes. Ind. Eng. Chem. Res., 45: 8749-8756.

Chowdhury, M., M.G. Mostafa, T.K. Biswas and A.K. Saha, 2013. Treatment of leather industrial effluents by filtration and coagulation processes. Water Resour. Ind., 3: 11-22.

Costa, C.R. and P. Olivi, 2009. Effect of chloride concentration on the electrochemical treatment of a synthetic tannery wastewater. Electrochim. Acta, 54: 2046-2052.

Endres, F. and S.Z. El-Abedin, 2006. Air and water stable ionic liquids in physical chemistry. Phys. Chem. Chem. Phys., 8: 2101-2116.

Farmer, J.C., S.M. Bahowick, J.E.Harrar, D.V. Fix and R.E. Martinelli *et al*., 1997. Electrosorption of chromium ions on carbon aerogel electrodes as a means of remediating ground water. Energy Fuels, 11: 337-347.

Hordienko, V.O., V.S. Protsenko, S.C. Kwon, J.Y. Lee and F.I. Danilov, 2011. Electrodeposition of chromium coatings from Sulfate-carbamide electrolytes based on Cr (III) compounds. Mater. Sci., 46: 647-652.

Kuznetsov, V.V., E.G. Vinokurov and V.N. Kudryavtsev, 2001. Kinetics of electroreduction of $Cr3^+$ ions in sulfate solutions. Russ. J. Electrochem., 37: 699-703.

Langkam, J., 2011. Removal of chromium (VI) from water by using lanthanum based hybrid materials. Ph.D Thesis, Department of chemistry, National Institute of Technology, Rourkela, India.

Liu, Y.Z., D.X. Yuan, J.M. Yan, Q.L. Li and T. Ouyang, 2011. Electrochemical removal of chromium from aqueous solutions using electrodes of stainless steel nets coated with single wall carbon nanotubes. J. Hazard. Mater., 186: 473-480.

Meneses, E.S., M.L.P. Arguelho and J.P. Alves, 2005. Electroreduction of the antifouling agent TCMTB and its electroanalytical determination in tannery wastewaters. Talanta, 67: 682-685.

Protsenko, V. and F. Danilov, 2009. Kinetics and mechanism of chromium electrodeposition from formate and oxalate solutions of Cr (III) compounds. Electrochim. Acta, 54: 5666-5672.

Protsenko, V.S., F.I. Danilov, V.O. Gordiienko, S.C. Kwon and M. Kim *et al*., 2011. Electrodeposition of hard nanocrystalline chrome from aqueous sulfate trivalent chromium bath. Thin Solid Films, 520: 380-383.

Ram, B., P.K. Bajpai and H.K. Parwana, 1997. Characterisation and pretreatment of tannery wastewatera case study. Indian J. Environ. Prot., 17: 175-183.

Samir, D., 1996. Minimising the environmental impact of chromium tanning. Ph.D Thesis, Environmental Technology Department, Massey University, Palmerston North, New Zealand.

Song, Z., C.J. Williams and R.G.J. Edyvean, 2000. Sedimentation of tannery wastewater. Water Res., 34: 2171-2176.

Song, Z., C.J. Williams and R.G.J. Edyvean, 2004. Treatment of tannery wastewater by chemical coagulation. Desalination, 164: 249-259.

Song, Z., S.R. Edwards, K. Howland and R.G. Burns, 2003. Analysis of a retan agent used in the tanning process and its determination in tannery wastewater. Anal. Chem., 75: 1285-1293.

Surviliene, S., O. Nivinskiene, A. Cesunieneand A. Selskis, 2006. Effect of Cr (III) solution chemistry on electrodeposition of chromium. J. Appl. Electrochem., 36: 649-654.

Surviliene, S., V. Jasulaitiene, O. Nivinskienë and A. Cesuniene, 2007. Effect of hydrazine and hydroxylaminophosphate on chrome plating from trivalent electrolytes. Appl. Surf. Sci., 253: 6738-6743.