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REMOVAL COD IN TANNERY WASTE WATER: MODELLING BYTHE EXPERIMENTAL DESIGN

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ABSTRACT

This article is devoted to the experimental procedure followed for the treatment of industrial waste colored by coagulation flocculation. The amount of water used and therefore the volume of the effluent and its pollution rate vary considerably depending on the production step. The variations of the COD, of the effluents of different stages of the process of manufacturing the leather are evoked in this work.

A screening study is done in order to identify the most influential factors in COD as a response. Analytical methods and techniques will be presented.

Several factors such as pH, the nature of the coagulant, the concentration of the coagulant, the concentration of the flocculating agent, the concentration of the ash and the type of flocculantare taken into account in this study to determine their effects on The COD.

INTRODUCTION

In this study, a physicochemical characterization of the total effluent generated by the industrial unit of the city of Mohammedia chosen for the study was carried out in order to evaluate the pollution load emitted by the tannery in the environment.

Both by the nature of the materials disposed of and by the products used, beamhouse operations are the most heavily polluting and consume large quantities of water. Indeed, in terms of COD, almost 70% of the pollution is generated by pre-tanning operations [1].

The wastewater from the pre-quenching, quenching and re-greasing steps is slightly alkaline, rich in suspended solids and phosphorus and is loaded with COD with values that can exceed 4000 mg/l. The wastewater from the depilation stage is rich in suspended matter and also contains dissolved substances, sulphides, proteins and is overloaded with organic matter with COD between 20 and 30 g/l. [2] have shown that the unhairing-scutting process generates highly toxic and alkaline wastewater containing high concentrations of proteins, sulphides, suspended matter and salts. Finally, deliming effluents are less polluted and contain mineral salts. They are less rich in COD and phosphorus and have high levels of sulfate ions This article also presents the method of the experimental design followed for the physicochemical treatment of colored industrial tannery discharges by coagulation flocculation [3-4]. The supernatant is recovered for the determination of the COD of the treated wastewater.

Factors such as pH, the nature of the coagulant, the concentration of the coagulant, the concentration of the flocculant, the ash concentration and the type of flocculant are taken into account to determine their effects on COD. The results of the design of the experimental model are compatible with the experimental results.

The effluents used in our study undergo a simple decantation in two large basins before being discharged into the city's sewerage network. The reduction of pollution by simple decantation during one hour was studied for several companions of sampling. [5] studied the effect of decantation on the elimination of tannery effluent pollution. The results showed that 37.7% of the COD was removed by decantation for one hour.

MATERIALS AND METHODS

Sampling process

The wastewater comes from an industrial tannery unit located in the city of Mohammmedia. The sampling is carried out at the level of the effluents of each step of production and at the level of main collector where all the discharges of the industrial unit.

Two types of samples were taken: medium and spot samples. The average samples were obtained by manual mixing of samples taken at the end of each hour throughout a day. We wanted to ensure that the average samples represent the greatest possible diversity depending on the variability of the production program. Several sampling campaigns have been carried out.

The sampling is carried out at the level of the effluents of each stage of production and at the level of main collector where all the discharges of the industrial tanning unit.

Reagents

As coagulants, ferric chloride $FeCl_3$ and aluminum sulfate $Al_2(SO_4)_3$, being the most widely used reagents for the treatment of waste water by coagulation flocculation, were selected for this study.

To improve the removal efficiency of the flocculation coagulation pollution, flocculants are often used. The latter are organic or mineral, cationic, anionic or nonionic polymers and may be natural or synthetic. Seven flocculants of different natures were used in this study. These products have been provided free of charge by companies specializing in their production.

Analysis method

The COD expresses the amount of oxygen necessary to oxidize the organic matter (biodegradable or not) of a water with the aid of an oxidant. This parameter provides a more or less complete representation of the oxidizable materials present in the sample **[6]**.

It evaluates the quantity of organic matter by chemical analysis, by oxidation with an excess of potassium dichromate ($Cr_2O_4K_2$) in an acid environment, at high temperature (140-150 °C.) for 2 hours. It is expressed in milligrams per liter (mg/L) of oxygen.

Experimental process [7-9]

The flocculation coagulation tests were carried out under controlled laboratory conditions using a Jar test flocculator. For each test, four beakers of one liter each were used to examine the effect of the concentration of coagulant, flocculant, or coagulation pH.

Before each test, the wastewater is mixed well and appropriate volumes are transferred to the corresponding beakers.

For tests that involve the addition of the coagulant and the flocculant, after addition of coagulant, a known amount of flocculant is added and the rapid agitation is maintained for a further one minute. After rapid agitation, the mixture was slowly stirred for 20 min at 30 rpm. The coagulated wastewater is then transferred to Imhoff cones and allowed to settle for one hour.

Design of experiment method

The COD in (mg/L) chosen as an experimental response to evaluate the effect of different factors on the effectiveness of tannery wastewater treatment by coagulation flocculation, using the experimental design method is presented in figure below:

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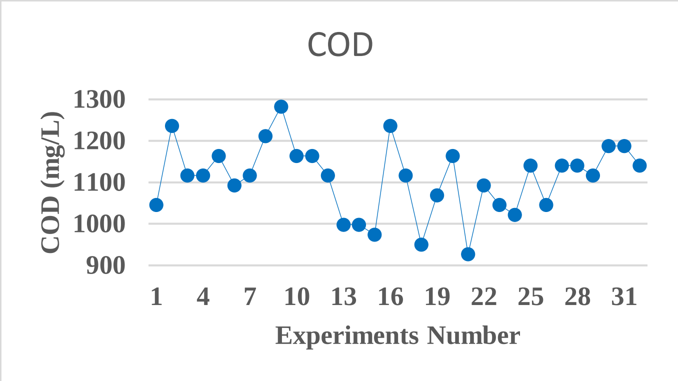

Fig. 1 : COD versus Experiments number

The COD measurements for the 32 experiments carried out are shown in figure 1.

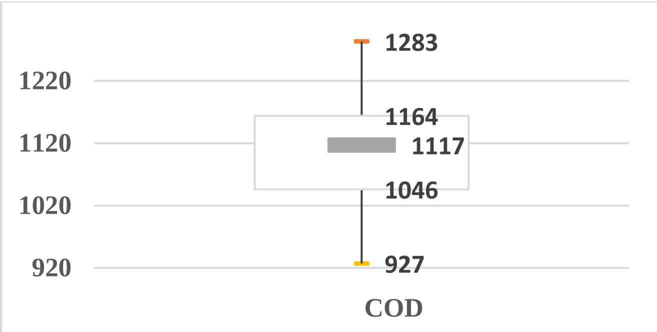

Fig. 2 : box-and-whisker chart

This box and whisker chart is based on five statistics coefficients that allows to summarize data: The value of the first quantile (1046), the value of the median (1117), the value of the third quartile (1164), and the two legs are used to summarize the data. lower (927) and upper (1283).

Factors definition

The factor definition step, carried out with the help of the Laboratory team, identified 6 potentially influential factors on COD. Five factors with two levels and one factor with seven levels. Table 1 summarizes the different modalities of the factors.

Table 1 Design variables and their levels

Factor	Factor Name	Level 1	Level 2	LeveI 3	Level 4	Level 5	Level 6	Level 7
X_1	Coagulant	Ferricchloride $FeCl_3$	Aluminun sulfate $Al_2(SO_4)_3$					
X_2	Coagulant concentration	250 mg/L	500 mg/L					
X_3	Flocculant concentration	0 mg/L	10 mg/L					
X_4	Ashes concentration	0 mg/L	100 mg/L					
X_5	pH	5	6					
X_6	Flocculant	P3000	Polyacrylamide	Astral Flocculant	Chimec 2063	Chimec 5161	Chimec 5264	Alginate

Where :

- Polysep 3000 (P3000), Cationic Organic Polymer Vegetable Origin - Chimec 2063, Polyamine in liquid form – Chimec 5161, Anionic polyelectrolyte powder - Chimec 5264, Cationic polyelectrolyte powder - Superfloc A-1820 (SU), Anionic polyacrylamide - Praestol 2515 TR, Copolymer of acrylamide and sodium acrylate and Alginate, natural polymer

Empirical model and its coefficients
In our case, we used an asymmetric screening matrix $2^5 7^1$ to study the weights (main effects) of the various factors. The experimental design developed corresponds to 32 experiments to be carried out.

The screening design makes it possible to determine the weight of the factors on the response of the system from an additive model by neglecting the interactions present between these factors.

The model we are looking for is therefore of the form:

$$Y = c_0 + c_1X_1 + c_2X_2 + c_3X_3 + c_4X_4 + c_5X_5 + c_6X_6 + c_7X_7 + c_8X_8 + c_9X_9 + c_{10}F_5X_{10} + c_{11}X_{11}$$

Where y represents the predicted response (COD en mg/L) and ci are the coefficients determined experimentally.

Table 2 Calculation of the estimation of ci effects

Coefficient	Value
c_0	1025,5
c_1	-34,2
c_2	34,1
c_3	55,2
c_4	-19,2
c_5	75,7
c_6	68,5
c_7	17,8
c_8	41,5
c_9	53,5
c_{10}	-29,7
c_{11}	11,8

The 12 coefficients of the mathematical model (table 2) make it possible to know the effect of the different factors.

RESULTS AND DISCUSSION

Statistical analysis of the model

Analysis of coefficients (Student test)

The Student's t-test allows us to estimate the probability that a coefficient is not significant from the ratio between the value of the coefficient and that of its standard error (the square root of its variance). The coefficients of variance correspond to the diagonal elements of the dispersion of the experimental matrix $({}^tXX)^{-1}$.

Table 3 : Statistical analysis of coefficients

Coefficient		VAR	Standard Error	t Stat	Significance P-Value %
c_0	1025,5	2008,072	44,812	22,885	0,000 <
c_1	-34,2	617,944	24,858	-1,376	18,410
c_2	34,1	617,944	24,858	1,372	18,533
c_3	55,2	617,944	24,858	2,221	3,809 <
c_4	-19,2	617,944	24,858	-0,772	44,893

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c_5	75,7	617,944	24,858	3,045	0,639 <
c6	68,5	1853,833	43,056	1,591	12,731
c7	17,8	2471,777	49,717	0,358	72,407
c8	41,5	2471,777	49,717	0,835	41,373
c_9	53,5	2471,777	49,717	1,076	29,470
c_{10}	-29,7	2471,777	49,717	-0,597	55,696
c_{11}	11,8	2471,777	49,717	0,237	81,480

Factors whose coefficients are c_3 and c_5 appear to be influential on the elimination of COD. Their influential character is confirmed by a new analysis of variance, presented in Table 3

Lenth Method

This graph below shows that no factor is active except pH. This does not mean that the results of mathematical analysis can not be exploited. It is preferable to analyze these results using another method such as Daniel's method or analysis of variance.

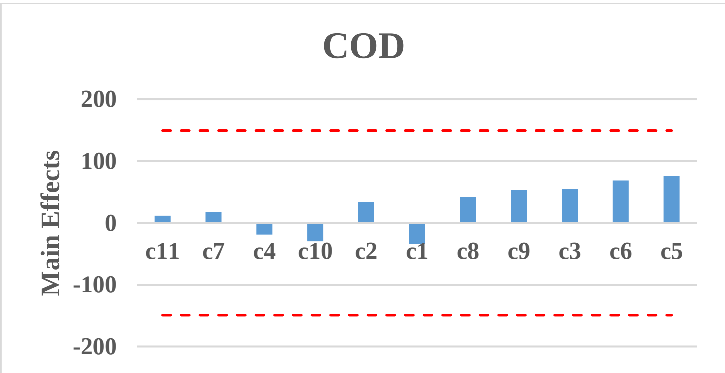

Fig. 3: Significant effects identified by Lenth's method

Daniel Method

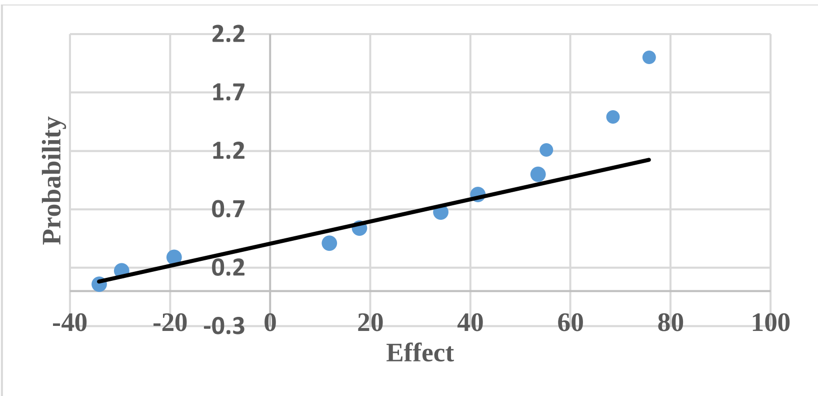

Figure 4: Significant effects identified by Daniel's method

The graph of Daniel (Normal half plot) allows to graphically test the normality of the distribution of the values of the effects. For this, their values are plotted on the abscissa axis, while the ordinates give a normal distribution probability scale (obtained by transforming a regular linear scale of values by using the normal inverse distribution function). If the distribution of the effect values is normal, the points thus transferred must align with a straight

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line. If an effect does not satisfy this condition, it means that it moves away from normality, and therefore it is likely to be significant. The corresponding factor may therefore be influential in this case (C_3 and c_5).

Analysis of variance (Ficher-Snedecortest)

ANOVA or ANalysis Of VAriance consists of comparing the experimental variances, the variances of the answers and the variances of the deviations. The Ficher-Snedecor test is represented in table 4.

The analysis of variance is probably the most rigorous of the statistical analysis methods used in this work.

Table 4 : Analysis of variance

Source of variation	Sum of squares	Degrees of Freedom	Mean Squares	F Ratio	Significance F
Regression (Model)	1.26146E+05	11	1.14678E+04	2.3198	4.92 < 5%
Residual	9.88711E+04	20	4.94355E+03		
Total	2.25017E+05	31			

We obtain for the response a very low value of significance which leads to the validation of the proposed model.

Graphical method

Main effects plot

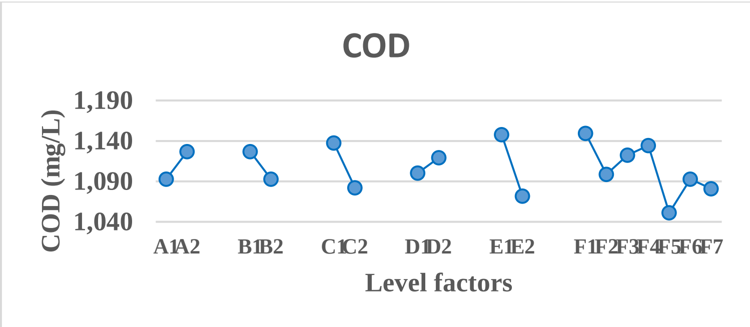

Fig. 5 **: Graphical representation of effects on COD**

The construction of the plot of the mean effects can be carried out from the calculation of simple arithmetic means. The mean effect of a factor is defined from the observed difference of a response variable, when this factor undergoes a change in modality. The plot of the average effects facilitates the visualization of the average effects.

Pareto chart

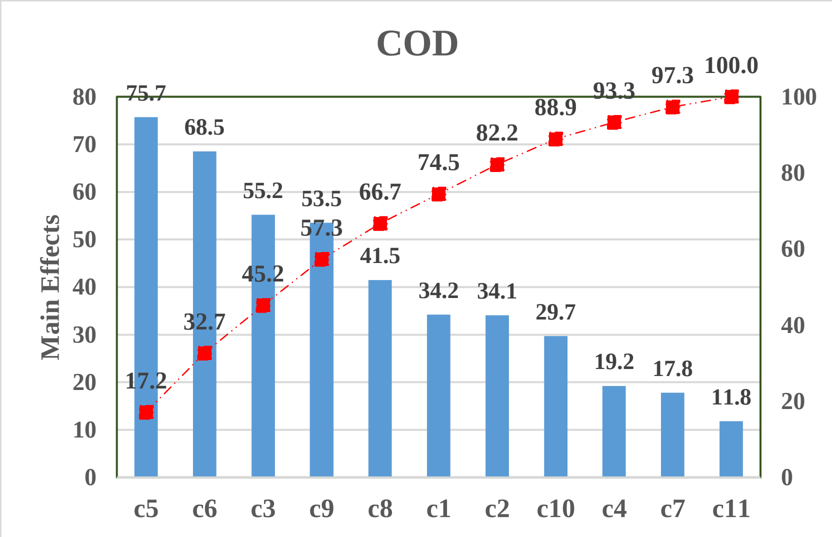

Fig. 6: PARETO chart of factors effects

In this example, we see that the effect of factors c5, c6, c3 and c9 is important and contributes to explaining nearly 53.5% of variations in response (COD). On the other hand, factors c4, c7 and c11 do not appear to be significant. It is then necessary to verify that these factors are not involved in an interaction, if not, these factors can be removed from the study.

Model validation

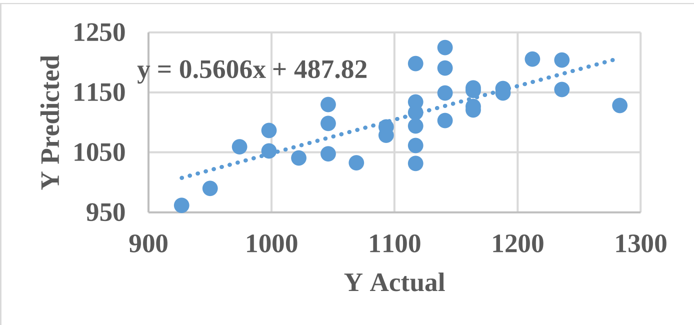

Fig. 7 : Model validation graph

The representation of the first bisector makes it possible to visualize a judgment on the alignment of the points: the closer the cloud is to this first bisector, the better the model describes the variation of the test results. The suitability graph then makes it possible to graphically translate the descriptive quality of the model as shown in Figure 7 in the case of COD measurements.

In addition, table 4 ANOVA confirms the pattern matching graph.

After adjustment of the pH to its optimal value, increasing doses ranging from 50 to 1200 mg/l of $FeCl_3$ have been tested for the removal of COD. The results show that ferric chloride is effective for the removal of COD from tanning effluents.

The COD removal rate is considered to be satisfactory, taking into account that 50% elimination is suggested as an optimum value for the chemical treatment of tannery wastewater **[10]**. However, the COD content of the treated wastewater obtained in this study reveals that with a large initial load, the abatement is unsatisfactory.

Aluminum sulfate has also been tested for the treatment of tannery wastewater. Jar tests were conducted at optimum pH, with increasing doses of $Al_2 (SO_4)_3.18H_2O$ that goes from 50 to 1200 mg/L. Treatment performance was evaluated by COD removal efficiencies

The results show that aluminum sulfate is effective for the removal of COD from tanning effluents. The coagulant effect on COD removal shows that the elimination rate increases with the coagulant concentration to a maximum at the optimum aluminum sulfate value. Above this value, the elimination rate remains unchanged or decreases slightly.

The polysep 3000 (P3000) is a natural organic flocculant based on acidified vegetable tannins and can replace inorganic salts for wastewater treatment

Flocculation coagulation tests were conducted to evaluate the effect of P3000 on the elimination of COD. Differents concentrations of flocculants goes from 10 to 1200 were tested.

The effect of P3000 shows that it is effective for the removal of COD from tanning effluents. COD decreases with increasing flocculant concentration to a minimum at the optimum of P3000; Beyond this concentration the removal efficiency remains almost unchanged.

The determination of the type of coagulant and its optimum dose must not only improve the characteristics of the waters but also reduce the cost of treatment. Treatment of tannery discharges has shown that the COD removal efficiency depends on the reagent used. Ferric chloride is less expensive, while the use of P3000 is relatively expensive.

The results show that the rate of pollution elimination and the amount of sludge generated using aluminum sulfate and chimec flocculant 5161 depend on the characteristics of the raw effluent. 40 to 74% of the COD and 40 to 89% of the color is eliminated. These results are very satisfactory and allow to have a water respecting the Moroccan standards of rejection. The addition of the flocculant, in addition to coagulant, makes it possible to improve the efficiency of removal of the COD.

CONCLUSION

The physicochemical characterization of the total effluent discharged by the tannery has shown that these discharges are complex, very laden with organic and mineral matter, have variable characteristics over time and are not easily biodegradable. Indeed high concentrations, which exceed the standard values in COD are observed. The COD contents during the different sampling compartments show values above the limit value set by the draft Moroccan standards for indirect discharge (1000 mg / L). This high loading of oxidizable materials is mainly due to the biogenic materials of the skins and to the organic chemicals used during the process of transformation of the skins. The beamhouse workshop remains the main process that contributes to this high organic matter load, particularly the unhairing-scutting stage, which generates effluents that are too COD-loaded with values up to 27 g / l. To get an idea of the variation in COD during the day, four daily follow-ups were performed. The results thus obtained showed that the COD contents ranged from 700 to 3400 mg/L.

Maximum COD values were observed at 12 o'clock, which is related to the discharge from the river workshop, which is often done at this time of day. These COD contents are comparable to the results obtained by [11-15], and remain reliable with respect to the values reported by [16 -18] which showed that the pollutant content can vary between 27 and 30 g/COD.

The analysis of the results of screening design made it possible to highlight the factors influencing the process of coagulation flocculation. The treatment of tannery effluents is effective at pH = 6 using aluminum sulfate at 500 mg / L and flocculant chimec 5161 at 10 mg / L.

REFERENCES

1. T. Ramasami T. and al., "Beamhouse and tanning operations: process chemistry revisited". JE Soc. Leather Technol. Chem. 83, pp. 39-45, 1999.
2. K. Cooman, M. Gajardo, J. Nieto, C. Bornhardt, G. Vidal, "Tannery characterization and toxicity effects on Daphnia" spp. Environ. Toxicol. Pp. 17, 45 – 51, 2003.
3. M. Assou, L. El Fels, A. El Asli, H. Fakidi, S. Souabi & M. Hafidi "Landfill leachate treatment by a coagulation–flocculation process: effect of the introduction order of the reagents" Desalination and Water Treatment 2016
4. M. Assou, A. Madinzi, A.Anouzla, M.A. Aboulhassan, S. Souabi, M. Hafidi, "Reducing Pollution of Stabilized Landfill Leachate by Mixing of Coagulants and Flocculants: a Comparative Study", International Journal of Engineering and Innovative Technology (IJEIT) Volume 4, Issue 1, July 2014
5. Z, Song, C.J. Williams, R.G.J.Edyvean, "Sedimentation of tannery wastewater". Water Res. Vol. 34, pp. 2171-2176, 2000.
6. AFNOR, « La qualité de l'eau, Recueil Environnement ». Association Française de Normalisation, Paris, France, 1999.
7. M. Assou, A. Madinzi, M. A. Aboulhassan and S. Souabi, "Removal of Turbidity in Tannery Waste Water: Modelling by the Experimental Design" International Journal of Civil and Environmental Engineering, ISSN:1701-8285, Vol.36, Issue.2 september 2014
8. F. Rabier, Modélisation par la méthode des plans d'expériences du comportement dynamique d'un module IGBT utilisé en traction ferroviaire, Thèse de Doctorat de l'Institut National Polytechnique de Toulouse, 2007.
9. S. Karam, Application de la méthodologie des plans d'expériences et de l'analyse de données à l'optimisation des processus de dépôt, thèse de Doctorat Faculté des Sciences et Techniques, Université de Limoges, 2004.
10. Talinli I and al., "Pretreatment of tannery wastewater", Water Sci. Technol. 29, pp. 175-178, 1994.
11. J.I Garrote, M. Bao, P. Castro, M.J. Bao "Treatment of tannery effluents by a two step coagulation flocculation process" Water Res., 29, pp. 2605–2608, 1995.
12. B Ram., K.B and al., « Kinetics of chrome-tannery effluent treatment by the activated-sludge system". Process Biochem., Vol. 35, pp. 255-265, 1999.
13. Iaconi C.D., Lopez A., Ramadori R.Di Pinto A.C. and Passino R., "Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR)". Wat. Res. 36, pp. 2005-2214, 2002.
14. M.Murugananthan, G.R.Bhaskar, S.prabhakar, "Separation of pollutants from tannery effluents by electro flotation". Separation and Purification Technology Vol. 40 2004, pp. 69-75, 2004.
15. O Lefebvre., N. Vas ude van, M. Torri jos z, K. Thanasekara n et R. Mole, " Halophilics biological treatment of tannery soak liquor in a sequencing batch reactor". *Water Res.*, Vol. 3, 2005.
16. Vlyssides G.A.et Israilides J.C., "Detoxification of tannery wastewater liquids with an electrolysis system". Environmental pollution 97 (1997) pp. 147-152, 1997.
17. Meric S. and al., "Toxicity of leather tanning wastewater effluents in sea urchin early development and in marine microlage". Chemosphere 61 (2005) pp. 208-217, 2005.
18. E.Genschow, W.Hegemann, C.Aschke, "Biological sulfate removal from tannery wastewater in a twostage anaerobic treatment". Wat. Res. Vol. 30, 1996, pp. 2072-2078, 1996.