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# Modelling by the experimental design for color removal (absorbance at 254 nm) from tannery wastewater

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**ABSTRACT**

This article is devoted to the results obtained during the physicochemical treatment of colored industrial tannery discharges of the city of Moahammedia by coagulation flocculation. The volume of settled sludge is measured and the supernatant is recovered for the determination of the color of the treated water, this one is measured on samples previously filtered through fiber membranes. The effectiveness of color removal was investigated by measuring the absorbance at 254 nm. We were interested in the application of the methodology of screening experimental designs on the parameters that influence the color of treated water. Six factors with different modalities were identified, such as: five factors (coagulant, coagulant concentration, flocculant concentration, ash concentration and pH) with two levels, and one factor (flocculant) with seven levels. The influence of these parameters on a response accommodated at the exit was highlighted. The derivation of a theoretical model has been realized. A series of experiments is carried out. The analysis of our results, based on a statistical approach, is presented. The parameters that have a significant influence on the outputs have been identified. Thus, the input factors such as: coagulant and pH have a large influence on the measured response at the outlet (the absorbance at 254 nm). This allowed the validation of the model. The theoretical and experimental results are very convergent. Furthermore, the results of our paper demonstrated that the approach used is promising in terms of the low time, cost and equipments; that have been used to carry out the test.

*Keywords:* Experimental design; Screening; Tannery wastewater; Absorbance

## 1. Introduction

Tannery effluents are often colored as a result of the discharge of the effluents from the dyeing operation, the role of which is the chemical fixation of dyes on the fibers [1,2]. Dyestuffs are characterized by their ability to absorb light radiation in the visible spectrum (from 380 to 750 nm). The transformation of white light into colored light by reflection on a body or by transmission or diffusion results from the selective absorption of energy by certain groups of atoms called chromophore; The coloring molecule being the chromogen. In a water sample, there are two types of color; the apparent color due to dissolved substances and suspended matter, and the true color which is due solely to dissolved substances [3].

In this study we are interested in true or real color. The flocculation coagulation was tested for the treatment of two tannery samples [4,5]. The first sample is taken from an instantaneous sample and the second sample consists of different samples taken during one day. The objective of this work is to study the possibility of reducing the pollution of certain tannery colored waste by techniques that

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are easy to exploit, less costly in production and operation and requiring less space. Thus, the flocculation coagulation treatment processes have been employed to combat the pollution of colored industrial discharges, such as liquid discharges from the tanning industry [4]. The main advantage of the conventional methods of treatment is that the discoloration of the wastewater coloration is due to the removal of the dye molecules and not to their partial decomposition which can give rise to toxic aromatic compounds [5]. As the absorbance measurement indicates the elimination of the color, a screening study [6–8] is carried out on response (absorbances at 254 nm), in order to identify the most influential factors on the elimination of the color. Static features and graphical methods will be presented.

## 2. Materials and methods

### *2.1. Sampling process and analysis method*

The wastewater comes from an industrial tannery unit located in the town of Mohammedia [1]. 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 plant lead. 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.

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 elimination 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. The different flocculants are:

Polysep 3000 (P3000), cationic organic polymer vegetable origin - Chimec 2063, polyamine in liquid form – Chimec5161, anionic polyelectrolyte powder - Chimec5264, cationic polyelectrolyte powder - Superfloc A-1820 (SU), anionic polyacrylamide - Praestol 2515 TR, copolymer of acrylamide and sodium acrylate - alginate, alginate, natural polymer.

For the physicochemical characterization of raw and treated wastewater, different parameters were determined according to standard spectrophotometric methods [5,9,10]. The absorbance is measured using a UV-visible spectrophotometer (model 7800 UV/VIS) of 2 nm bandwidth and double beam. The tanks used are in quartz (optical path 1 cm). The precision on the absorbance measurement between 200 and 1000 nm is 1 unit [9]. The spectrophotometer was used to evaluate color in the visible range and to monitor soluble organic pollution at wavelengths of 254 nm. Before the color measurement, the sample is filtered on a 0.45 µm glass fiber membrane. Of pore diameter to remove suspended solids. Since wastewater contains various kinds of dyes and pigments (depending on production), the traditional method which applies the absorbance at the maximum absorption wavelength is not used. The color is determined using a UV/Visible spectrophotometer [1,2], (Model 7800 UV/VIS spectrophotometer) by measuring the absorbance at the wavelength 254 nm and the color correspond to this absorbance. 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 involving the addition of coagulant and flocculant, after the addition of coagulant, a known amount of flocculant is added and rapid stirring is continued for a further one minute. After rapid stirring, 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 1 h.

### *2.2. Design of experiment method*

As previously stated, the experimental response of tannery wastewater treatment by coagulation flocculation observed in this study is the color, which corresponds to the sum of the absorbance at wavelength 254 nm.

The figure below of the box-and-whisker chart, shows the distribution of the numerical values of the chosen variable (the absorbance at 254) (Fig. 1).

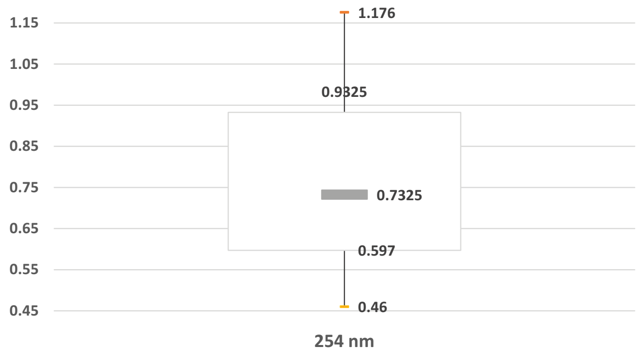


Fig. 1. Box-and-whisker chart.

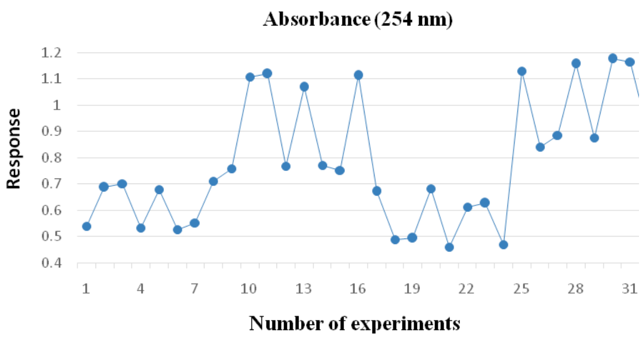


Fig. 2. Variation of response during the experiments.

For this absorbance, the value of the first quantile is 0.597, the median value is 0.7325, the third quartile value is 0.9325.

The color corresponding to the absorbance at the wavelength 254 nm, varies enormously during the experiments carried out.

### 2.3. Definition of factors

The step of definition of factors, carried out with the help of the Laboratory team, identified six factors potentially influencing the color of the treated water.

The experimental domain consists of the set of possible combinations of factors. In our case, we studied six factors with different number of modalities. Five factors (coagulant, coagulant concentration, flocculant concentration, ashes concentration and pH) with 2 levels and 1 factor (flocculant) with seven levels (Table 1).

It can be seen from Fig. 3, that the coagulant and pH (factors A and E) clearly influence the color that corresponds to the absorbance at the wavelength 254 nm. This phenomenon is highlighted on the Pareto diagram.

### 2.4. Empirical model and its coefficients

As variables do not have the same number of levels, we have chosen an asymmetric screening experiments matrix with 32 experiments. The mathematical model used in this screening study is therefore a polynomial model of the first degree, neglecting the calculation of the interactions present between these factors, and it can be represented by the equation:

$$Y = Cste + A_1X_1 + B_1X_2 + C_1X_3 + D_1X_4 + E_1X_5 + F_1X_6 + F_2X_7 + F_3X_8 + F_4X_9 + F_5X_{10} + F_6X_{11}$$

where Y represents the observed response (Color).

The model has twelve unknowns to be determined. These twelve coefficients make it possible to know the effect of the various actors.

## 3. Results and discussion

### 3.1. Statistical analysis of the coefficients

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.

Factors whose coefficients are $A_1$ and $E_1$ seem to influence the color.

### 3.2. Statistical analysis of the model

The Lenth method consists in estimating a pseudo-standard error to implement a statistical test, the result of which is the plotting of the significance limits on the bar graph.

Fig. 4 shows that the factors: the coagulant (coefficient A1) and the pH (coefficient E1) are active for the absorbance at 254 nm. This does not mean that the results of mathematical analysis cannot be exploited. It is preferable to analyze these results using another method such as Daniel's method or analysis of variance.

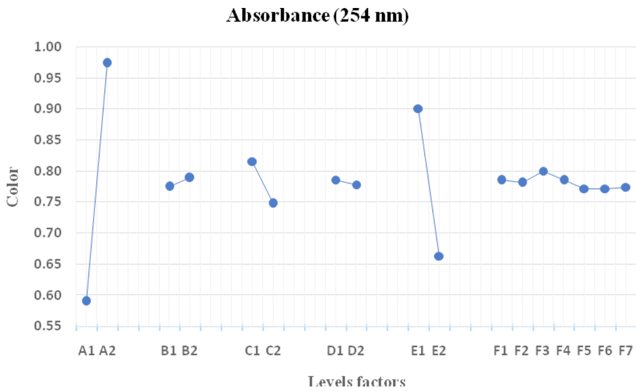


Fig. 3. The effects of the parameters on the response.

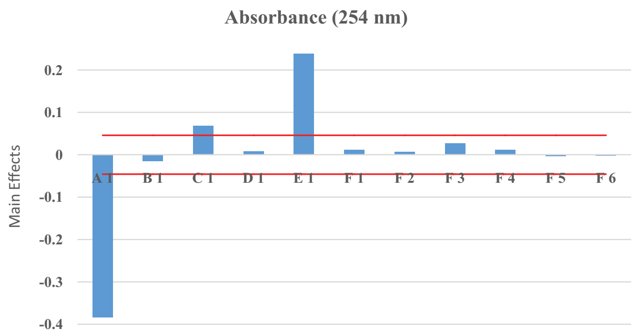


Fig. 4. Significant effects identified by Lenth's method (Absorbance 254 nm).

Table 1
Design variables and their levels

| Factors | Factors name | Number of level | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 | Level 6 | Level 7 |
|---|---|---|---|---|---|---|---|---|---|
| $X_1$ | Coagulant | 2 | $Al_2(SO_4)_3$ | $FeCl_3$ | | | | | |
| $X_2$ | Coagulant concentration | 2 | 250 | 500 | | | | | |
| $X_3$ | Floculant concentration | 2 | 0 | 10 | | | | | |
| $X_4$ | Ashes concentration | 2 | 0 | 100 | | | | | |
| $X_5$ | pH | 2 | 5 | 6 | | | | | |
| $X_6$ | Floculant | 7 | P3000 | Polyacryl-amide | Floculant Astral | Chimec 2063 | Chimec 5161 | Chimec 5264 | Alginate |

Table 2
Calculation of the estimation of ai effects

| Designation | Cste | $A_1$ | $B_1$ | $C_1$ | $D_1$ | $E_1$ | $F_1$ | $F_2$ | $F_3$ | $F_4$ | $F_5$ | $F_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 254 nm Coefficient | 0.8167 | 0.3839 | 0.0144 | 0.0679 | 0.0079 | 0.2376 | 0.011 | 0.007 | 0.026 | 0.0108 | 0.0027 | 0.0025 |

Table 3
Statistical analysis of coefficients (Absorbance 254 nm)

| Coefficient | | Standard Error | t Stat | Significance P-Value % |
|---|---|---|---|---|
| Cste | 0.8167 | 0.033 | 24.76 | < 0.01 *** |
| $A_1$ | –0.3839 | 0.0183 | –20.98 | < 0.01 *** |
| $B_1$ | –0.0144 | 0.0183 | –0.79 | 44.7 |
| $C_1$ | 0.0679 | 0.0183 | 3.71 | 0.146 ** |
| $D_1$ | 0.0079 | 0.0183 | 0.43 | 67.4 |
| $E_1$ | 0.2376 | 0.0183 | 12.99 | < 0.01 *** |
| $F_1$ | 0.011 | 0.0317 | 0.35 | 73.1 |
| $F_2$ | 0.007 | 0.0366 | 0.19 | 84.4 |
| $F_3$ | 0.026 | 0.0366 | 0.71 | 49.2 |
| $F_4$ | 0.0108 | 0.0366 | 0.29 | 76.9 |
| $F_5$ | –0.0027 | 0.0366 | –0.08 | 93.9 |
| $F_6$ | –0.0025 | 0.0366 | –0.07 | 94.4 |

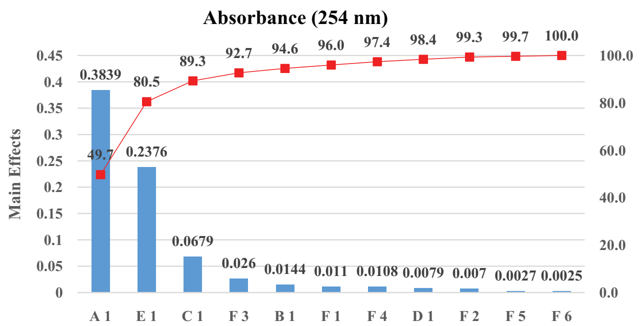


Fig. 5. Pareto chart of factors effects (Absorbance 254 nm).

Fig. 5 shows that the three factors listed above (coagulant, flocculant and pH) influence the absorbance at 254 nm.

The results show that the absorbances at 254 nm are influenced significantly by the coagulation pH and the nature and concentration of coagulant used. The results show that the pH and the nature of the coagulant used have a significant effect on the volume of the sludge formed. Coagulation flocculation generates less sludge at pH = 5 and using aluminum sulfate. However, the removal of organic matter and the color of the wastewater is effective at pH = 6.

### 3.3. Analysis of variance (Ficher-Snedecor test ANOVA)

The application of ANOVA to the same results obtained for the response (Absorbance 254 nm) led to the analysis table of the variance given in Table 4.

The probability of the response is very low, so the model is valid for the absorbance at 254 nm.

### 3.4. Graphical method

The results of Fig. 6 illustrate the comparative study between the value measured at 254 nm and the calculated value. These results indicate that the two results are comparable.

The indicators reflect the descriptive quality of the models that appear to reflect the values measured of the color (absorbance at 254 nm). A graphical analysis of the results and more precisely of these graphs of adequacy will allow to observe this quality. In addition, the ANOVA (Table 4) chart confirms the model adequacy graphs (the coefficient of determination $R^2$ is very close to unity).

## 4. Conclusion

Color is one of the major problems in wastewater and many techniques can be applied to eliminate them [1,2,11]. A methodology for the experimental design and response surface of 32 is used to optimize the process of coagulation-flocculation Release tannery industry to reduce the cost and the number of experiments and enhance the process on an industrial scale [12,13].

Test campaigns are organized in a well-defined logic. According to the experiments approach, numerical computation the results of these measurements are processed using statistical and algebraic rules to reduce the effect of each factor. After that, we proposed an analytical table of the variance in order to appreciate the influence of the detailed impact of each factor.

In order to compare the results obtained with each reagent used, a study, based on the pollution elimination efficiencies corresponding to the optimal dose of each reagent, was carried out.

The study of the effect of the coagulants and the flocculant used on the efficiency of treatment of tannery rejects showed that the color depends on the reagent used [9,14]. However, in choosing a treatment pathway, one must consider both the normative objectives to be achieved and the cost of treatment. To compare the results obtained with each coagulant, the color removal efficiency was estimated considering the organic matter removal and color performance. Aluminum sulfate produces less sludge for a given yield of COD or color [15,16].

Based on the cost of coagulants, ferric chloride remains the least expensive reagent. However, it produces more turbid water compared to other reagents and eliminates less color and chromium compared to aluminum sulfate. Thus, the latter is more attractive for the treatment of wastewater in the tanning industry. Indeed, this reagent allows higher pollution removal efficiencies, generates quantities of non-excessive sludge and the cost of its use is relatively average.

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 charac-

Table 4
Analysis of variance (Absorbance 254 nm)

| Source of variation | Sum of squares | Degrees of Freedom | Mean Squares | F Ratio | Significance F |
|---|---|---|---|---|---|
| Regression | 1.672 | 11 | 0.1520 | 56.763 | 1.28547E-12 <0.01% |
| Residues | 0.054 | 20 | 0.0027 | | |
| Total | 1.726 | 31 | | | |

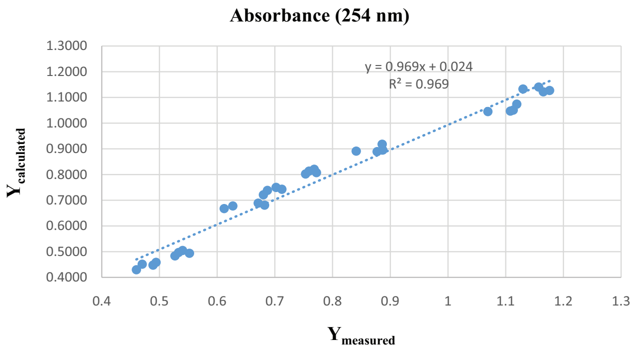


Fig. 6. Model validation (absorbance 254 nm).

teristics of the raw effluent. This procedure allowed us to eliminate 40 to 89% of the color, which is one of the main problems of wastewater.

As a result, the coagulation-flocculation technique is necessary to reduce wastewater pollution. Thus, the results obtained are very satisfactory and allows to have a water respecting the Moroccan standards of rejection [9,15]. The effectiveness of the used research method offers the possibility to include some additional design factors in a new research for the optimum.

## References

[1] M. Assou, A. Madinzi, B. Lachgar, Souabi, Removal color from tannery waste water: modelling by the experimental design, I.J.E.S.R.T, 6 (2017) 537–548.

[2] M. Assou, B. Lachgar, A. Madinzi, Souabi, Removal COD in tannery waste water: modelling by the experimental design, G.J.E.S.R.M, 4 (2017) 102–110.

[3] M. Assou, B. Lachgar, A. Madinzi, S. Souabi, Formed sludge in tannery wastewater : modelling by the experimental design, I.J.S.E.I , 6 (2017) 103–107.

[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, I.J.E.I.T, 4 (2014) 20–25.

[5] S. Jeffery-Black, S.J. Duranceau, The influence of solute polarizability and molecular volume on the rejection of trace organics in loose nanofiltration membrane processes of trace organics in loose nanofiltration membrane processes, Desal. Water Treat., 57 (2016) 29059–29069.

[6] S. Karam, Application de la méthodologie des plans d'expériences et de l'analyse de données à l'optimisation des processus de dépôt (Application of the methodology of the plans of experiments and the analysis of data to the optimization of the processes of deposit), Limoges, 2004.

[7] D. Nawal, T. Habib, H. Mouloud, Application de la méthode de Taguchi pour l'étude des sols gonflants (Application of the Taguchi method for the study of swelling soils), HAL, (2015) 1–7.

[8] S. Vivier, Stratégies d'Optimisation par la Méthode des Plans d'Expériences Et Application aux Systèmes Electrotechniques Modélisés par Eléments Finis (Strategies of Optimization by the Method of Plans of Experiments and Application to Electrotechnical Systems Modeled by Finite Elements), University of Science and Technology of Lille, 2002.

[9] J. Rodier, B. Legube, N. Merlet, L'Analyse de l'eau, 9ème éd., 2009, pp. 725–745.

[10] C.M. Van Genuchten, K.N. Dalby, M. Ceccato, S.L.S. Stipp, K. Dideriksen, Factors affecting the Faradaic efficiency of Fe(0) electrocoagulation, J.E.C.E, 5 (2017) 4958–4968.

[11] J. Guo, Y. Li, D. Hu, H. Liu, Preparation of transition-metal-doped ZnO nanophotocatalysts and their performance on photocatalytic degradation of antibiotic wastewater, Desal. Water Treat., (2014) 37–41.

[12] F. Rabier, Modélisation par la méthode des plans d'expériences du comportement dynamique d'un module IGBT utilisé en traction ferroviaire,(Modeling by the experimental design method of the dynamic behavior of an IGBT module used in railway traction), Thesis, National Polytechnic Institute of Toulouse, 2007.

[13] B. Wahdame, Analyse et optimisation du fonctionnement de piles à combustible par la méthode des plans d'expériences (Analysis and optimization of fuel cell operation by the experimental design method), University of Technology Belfort Montbeliard, 2006, Thesis.

[14] N.A. Sabri, H. Schmitt, B. Van der Zaan, H.W. Gerritsen, T. Zuidema, H.H.M. Rijnaarts, A.A.M. Langenhoff, Prevalence of antibiotics and antibiotic resistance genes in a wastewater effluent-receiving river in the Netherlands, J.E.C.E. (2018).

[15] B.M. Aboulhassan, M.A.S. Souabi, A. Yaacoubi, Treatment of textile wastewater using a natural flocculant, I.J.E.T, (2005) 705–711.

[16] M.O. Schwartz, Modelling groundwater contamination above a potential nuclear waste repository in the Columbia River Basalt , USA, I.J.E.E., 77 (2018) 1–12.