

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. The latter is measured on samples previously filtered through fiber membranes. The effectiveness of color removal was investigated by measuring the absorbance at 436, 525 and 620 nm. The aim of this work is to minimize the time, the cost and the means used to carry out the tests. The method of screening experimental designs was applied.

KEYWORDS: Experimental Design, Screening, Tannery wastewater, Absorbance.

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.

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. In this study we are interested in true or real color.

The flocculation coagulation [1 – 2] was tested for the treatment of two tannery samples. 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 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. The main advantage of the conventional methods of treatment is that the discoloration of the waste water coloration is due to the removal of the dye molecules and not to their partial decomposition which can give rise to toxic aromatic compounds [3].

As the absorbance measurement indicates the elimination of the color, a screening study is carried out on three responses (absorbances at 436 nm, 525 nm and 620 nm), in order to identify the most influential factors on the Elimination of the color. Static features and graphical methods will be presented.

MATERIALS AND METHODS

Sampling process and Analysis method

The wastewater comes from an industrial tannery unit located in the town of Mohammedia [4]. 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 $\text{Al}_2(\text{SO}_4)_3$, 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 - 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 - Alginate, Alginate, natural polymer

For the physicochemical characterization of raw and treated wastewater, different parameters were determined according to standard spectrophotometric methods. 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 1cm). The precision on the absorbance measurement between 200 and 1000 nm is 1 unit. The spectrophotometer was used to evaluate color in the visible range and to monitor soluble organic pollution at wavelengths of 254 nm, 436 nm, 525 nm and 620 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, (Model 7800 UV / VIS spectrophotometer) by measuring the absorbances at the three wavelengths 436, 525 and 620 nm and the color corresponds to the sum of these absorbances [5 – 6] 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 one hour.

Design of experiment method [7 – 8]

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 absorbances at wavelengths 436, 525 and 620 nm.

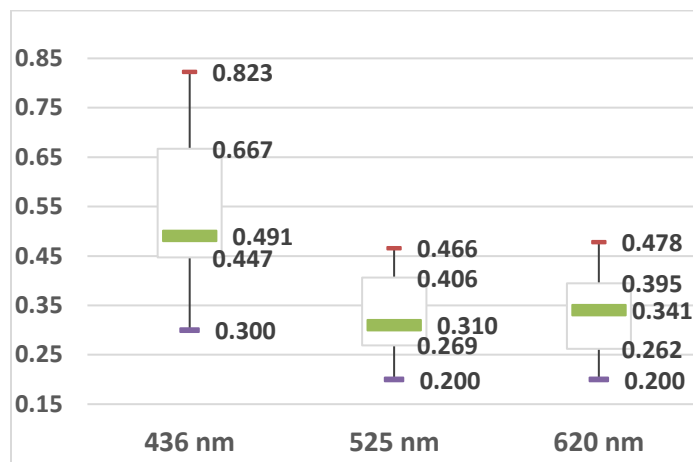


Fig. 1 : box-and-whisker chart

The box and whisker chart shows the distribution of the numerical values of the three variables chosen. For example, for absorbance at 525 nm, the value of the first quartile is 0.269, the median value is 0.310, the value of the third quartile is 0.406.

Factors definition

The factor definition step, carried out with the help of the Laboratory team, identified 6 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 study 6 factors with a different number of modalities. 5 factors (Coagulant, coagulant concentration, flocculant concentration, ashes concentration and pH) with 2 levels and 1 factor (flocculant) with 7 levels.

Table 1 Design variables and their levels

Factor	Factor Name	Level 1	Level 2	Level 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

Empirical model and its coefficients

As variables don't 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:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5 + a_6X_6 + a_7X_7 + a_8X_8 + a_9X_9 + a_{10}F_5X_{10} + a_{11}X_{11}$$

In which Y represents the observed response (Color).

The model has 12 unknowns to be determined. These 12 coefficients make it possible to know the effect of the various actors.

Table1: Calculation of the estimation of ai effects

Designation	436 nm Coefficient	525 nm Coefficient	620 nm Coefficient
a ₀	0,4115	0,2085	0,2049
a ₁	-0,0782	0,0188	0,0675
a ₂	0,0469	0,0325	0,0408
a ₃	0,0244	0,0115	0,0073
a ₄	-0,0003	-0,0004	-0,0017
a ₅	0,2292	0,1241	0,1179
a ₆	0,0418	0,0344	0,0234
a ₇	0,0475	0,0475	0,0408
a ₈	0,0565	0,0455	0,039
a ₉	0,0423	0,0338	0,0298
a ₁₀	0,0743	0,0595	0,0478
a ₁₁	-0,0037	-0,001	-0,002

RESULTS AND DISCUSSION

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.

Table 2.1: Statistical analysis of coefficients (Absorbance 436 nm)

Coefficient	VAR	Standard Error	t Stat	Significance P-Value %	
a ₀	0,4115	0,001	0,038	10,908	0,000<
a ₁	-0,0782	0,000	0,021	-3,737	0,130 <
a ₂	0,0469	0,000	0,021	2,241	3,653 <
a ₃	0,0244	0,000	0,021	1,166	25,736
a ₄	-0,0003	0,000	0,021	-0,014	98,870
a ₅	0,2292	0,000	0,021	10,952	0,000 <
a ₆	0,0418	0,001	0,036	1,153	26,243
a ₇	0,0475	0,002	0,042	1,135	26,985
a ₈	0,0565	0,002	0,042	1,350	19,213
a ₉	0,0423	0,002	0,042	1,011	32,426
a ₁₀	0,0743	0,002	0,042	1,775	9,109
a ₁₁	-0,0037	0,002	0,042	-0,088	93,044

Factors whose coefficients are a₁, a₂ and a₅ appear to influence color. Their influential character is confirmed by a new analysis of variance, presented in Table 2.1

Table 2.2: Statistical analysis of coefficients (Absorbance 525 nm)

Coefficient	VAR	Standard Error	t Stat	Significance P-Value %	
a ₀	0,2085	0,001	0,026	7,941	0,000 <
a ₁	0,0188	0,000	0,015	1,291	21,150
a ₂	0,0325	0,000	0,015	2,231	3,726 <

a ₃	0,0115	0,000	0,015	0,790	43,904
a ₄	-0,0004	0,000	0,015	-0,027	97,836
a ₅	0,1241	0,000	0,015	8,520	0,000 <
a ₆	0,0344	0,001	0,025	1,364	18,784
a ₇	0,0475	0,001	0,029	1,631	11,862
a ₈	0,0455	0,001	0,029	1,562	13,398
a ₉	0,0338	0,001	0,029	1,160	25,958
a ₁₀	0,0595	0,001	0,029	2,043	5,450
a ₁₁	-0,001	0,001	0,029	-0,034	97,296

Factors whose coefficients are a₂ and a₅ appear to influence color. Their influential character is confirmed by a new analysis of variance, presented in Table 2.2

Table 2.3: Statistical analysis of coefficients (Absorbance 620 nm)

Coefficient		VAR	Standard Error	t Stat	Significance P-Value %
a ₀	0,2049	0,001	0,024	8,392	0,000 <
a ₁	0,0675	0,000	0,014	4,983	0,007 <
a ₂	0,0408	0,000	0,014	3,012	0,688 <
a ₃	0,0073	0,000	0,014	0,539	59,587
a ₄	-0,0017	0,000	0,014	-0,126	90,137
a ₅	0,1179	0,000	0,014	8,704	0,000 <
a ₆	0,0234	0,001	0,023	0,997	33,048
a ₇	0,0408	0,001	0,027	1,506	14,767
a ₈	0,039	0,001	0,027	1,440	16,544
a ₉	0,0298	0,001	0,027	1,100	28,438
a ₁₀	0,0478	0,001	0,027	1,764	9,292
a ₁₁	-0,002	0,001	0,027	-0,074	94,188

Factors whose coefficients are a₁, a₂ and a₅ appear to influence color. Their influential character is confirmed by a new analysis of variance, presented in Table 2.3

Almost the same factors influence the three responses (Coagulant, concentration of coagulant and pH), remains to verify the influence of the concentration of coagulant

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.

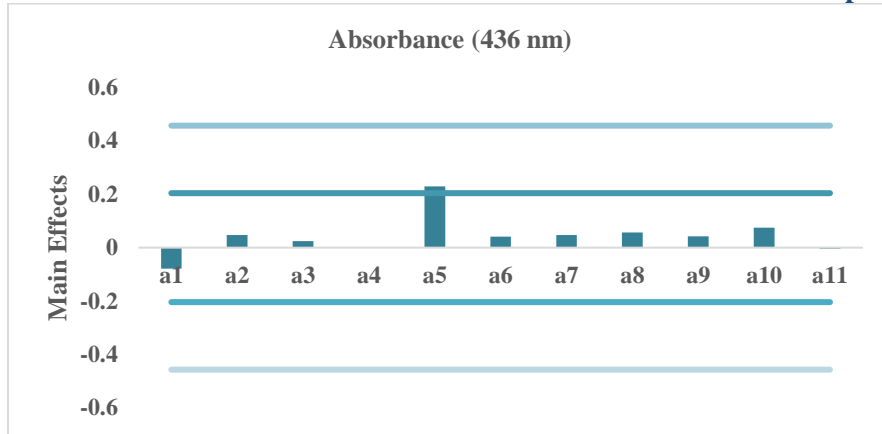


Fig. 2.1 : Significant effects identified by Lenth's method (Absorbance 436 nm)

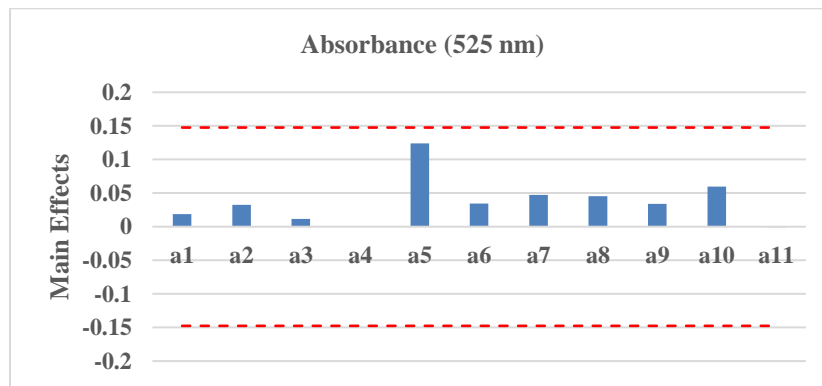


Fig. 2.2 : Significant effects identified by Lenth's method (Absorbance 525 nm)

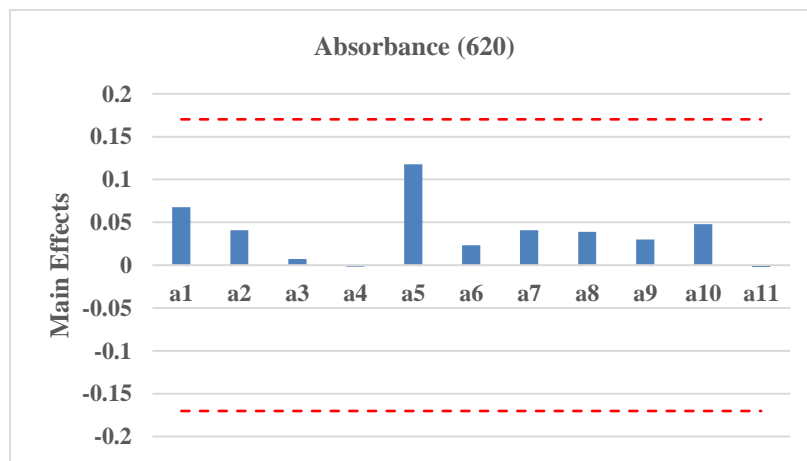


Fig. 2.3 : Significant effects identified by Lenth's method (Absorbance 620 nm)

These graphs show that no factor is active except pH (coefficient a_5) in the case of absorbance 436 nm only. 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.

These half-normal plots below show that pH is influent for the three absorbances.

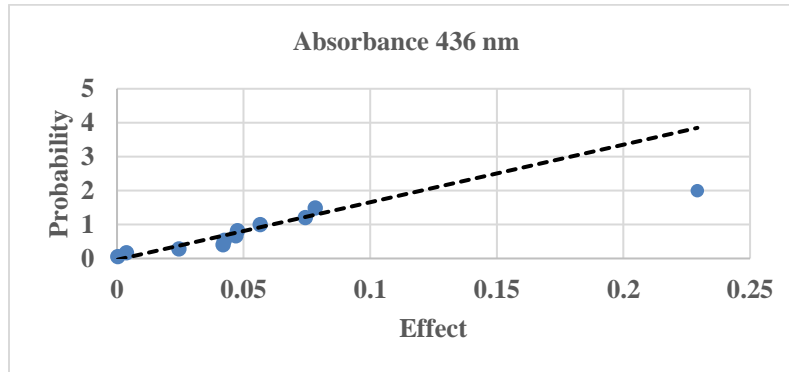


Fig. 3.1 : Significant effects identified by Daniel's method (Absorbance 436 nm)

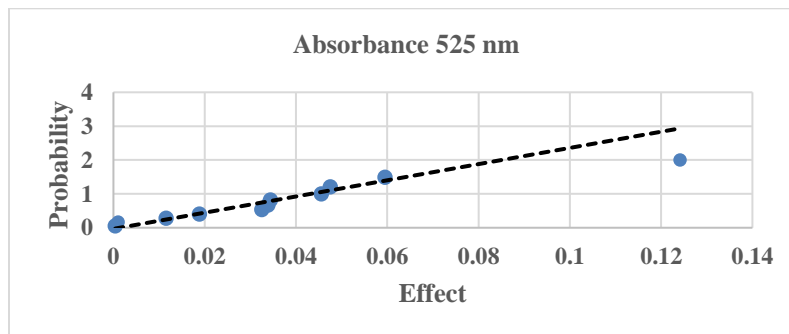


Fig. 3.2 : Significant effects identified by Daniel's method (Absorbance 525 nm)

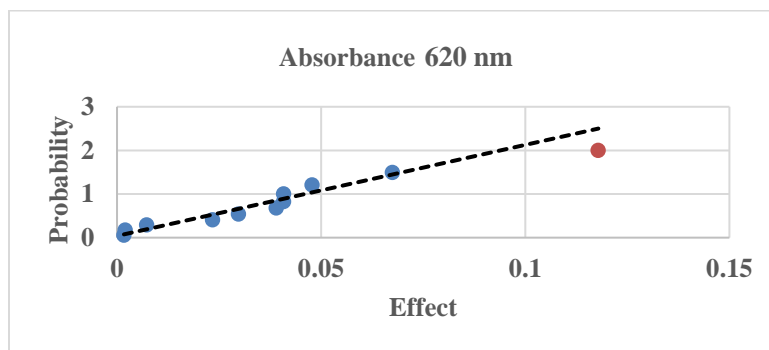


Fig. 3.3 : Significant effects identified by Daniel's method (Absorbance 620 nm)

Analysis of variance (Fischer-Snedecortest ANOVA)

The application of ANOVA to the same results obtained for the three responses (Absorbances at 436 nm, 525 nm and 620 nm) led to the analysis tables of variance given in tables 3.1, 3.2 and 3.3.

Table 3.1 : Analysis of variance (Absorbance 436 nm)

Source of variation	Sum of squares	Degrees of Freedom	Mean Squares	F Ratio	Significance F
Regression (Model)	0,511437	11	0,046494	13,270082	6,759E-07 <0,01%
Residual	0,070074	20	0,003504		
Total	0,581511	31			

Table 3.2 : Analysis of variance (Absorbance 525 nm)

Source of variation	Sum of squares	Degrees of Freedom	Mean Squares	F Ratio.	Significance F
Regression (Model)	0,148800	11	0,013527	7,970853	3,758E-05 <0,01%
Residual	0,033942	20	0,001697		
Total	0,182742	31			

Table 3.3 : Analysis of variance (Absorbance 620 nm)

Source of variation	Sum of squares	Degrees of Freedom	Mean Squares	F Ratio.	Significance F
Regression (Model)	0,170707	11	0,015519	10,573414	4,288E-06 <0,01%
Residual	0,029354	20	0,001468		
Total	0,200062	31			

The responses have a very low probability F, so the models are valid for the three absorbances.

Graphical method

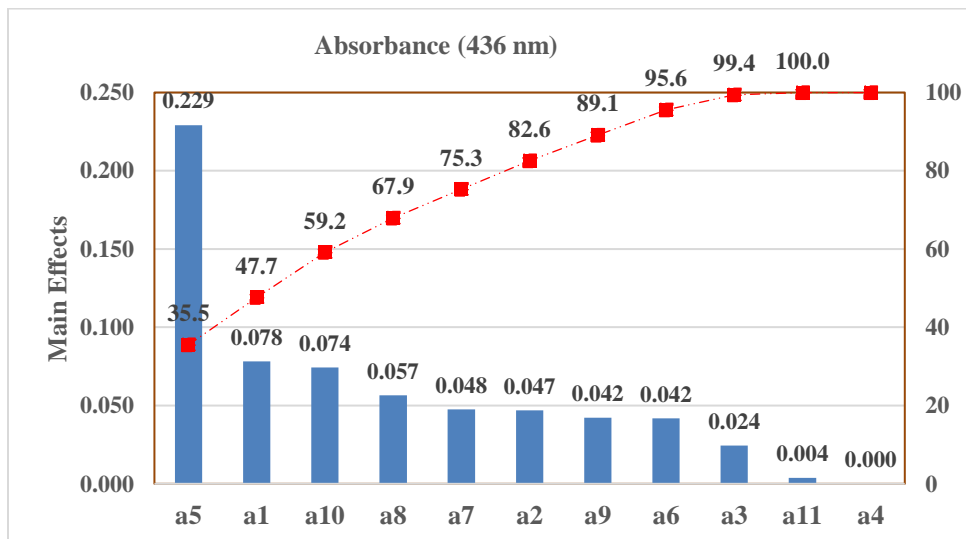


Fig. 4.1: PARETO chart of factors effects (Absorbance 436 nm)

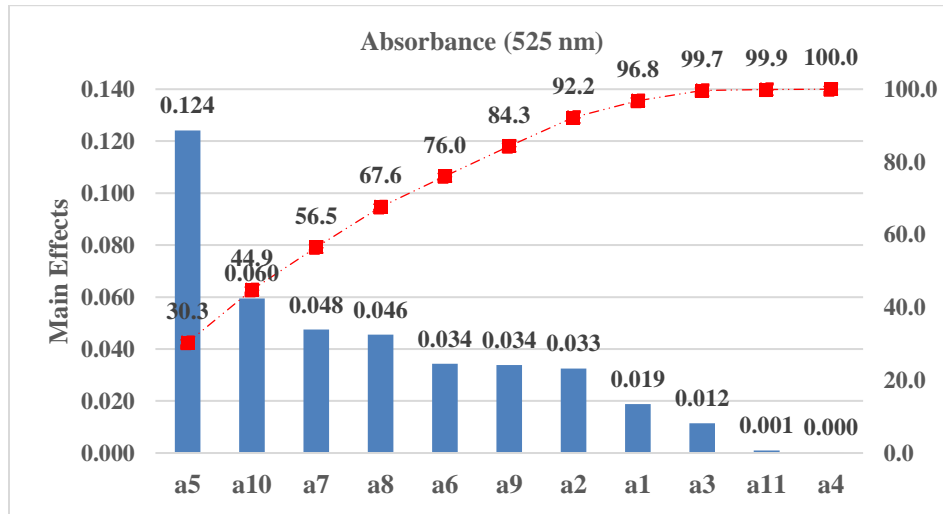


Fig. 4.2: PARETO chart of factors effects (Absorbance 525 nm)

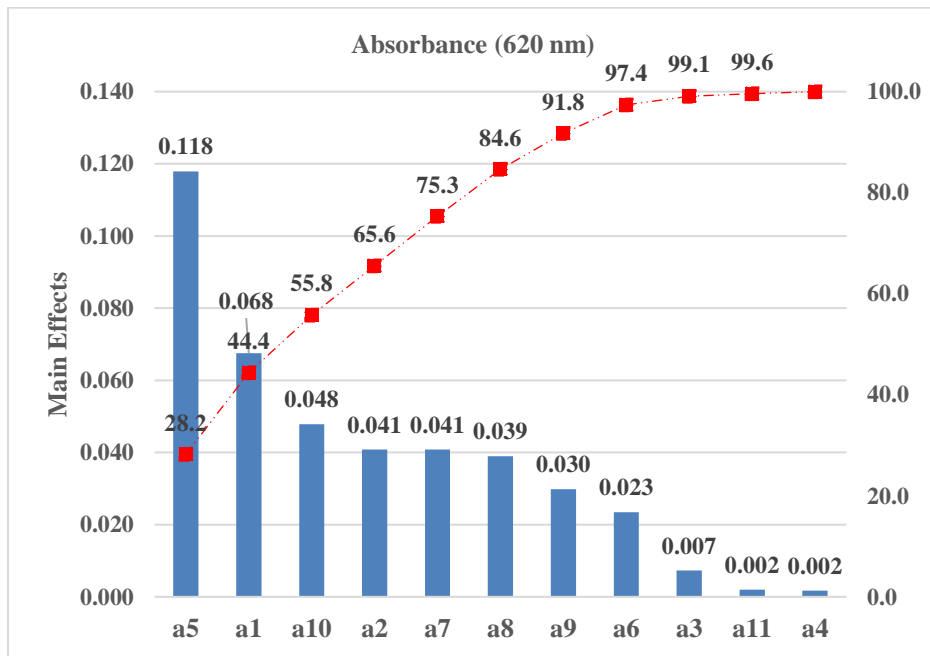


Fig. 4.3: PARETO chart of factors effects (Absorbance 620 nm)

The results show that the absorbances at 436, 525 and 620 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.

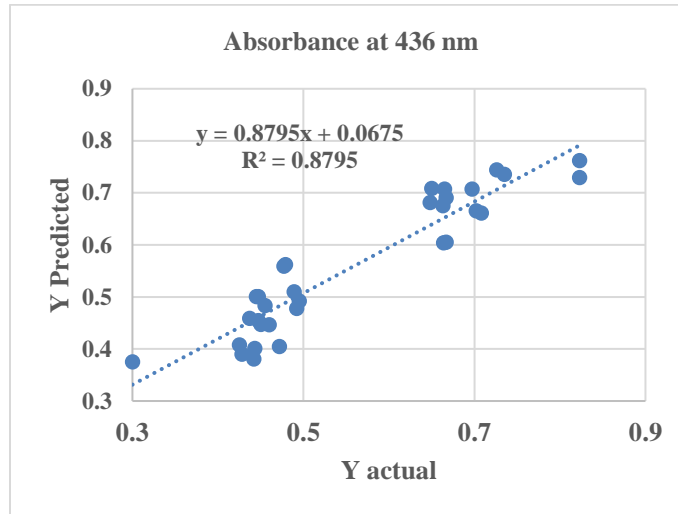


Fig. 5.1: Model validation (Absorbance 436 nm)

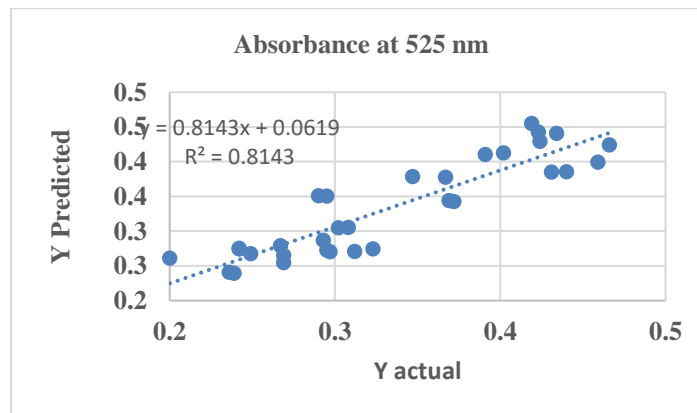


Fig. 5.2: Model validation (Absorbance 525 nm)

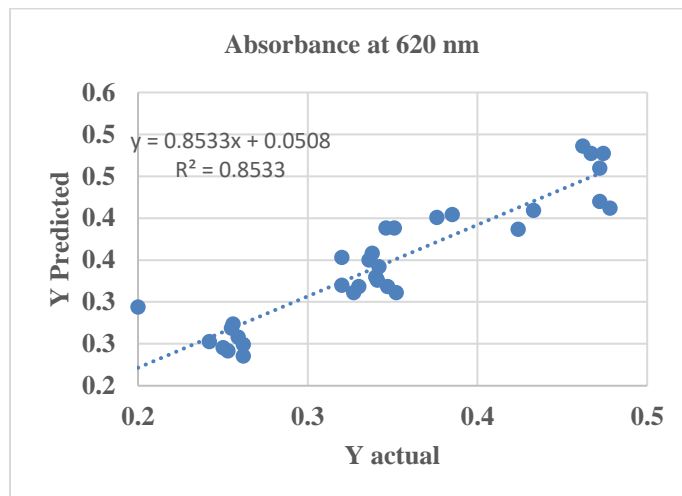


Fig. 5.3: Model validation (Absorbance 620 nm)

The indicators reflect the descriptive quality of the models that seem to reflect the measured values of color (Absorbance at 436, 525 and 620 nm). A graphical analysis of the results and more precisely these graphs of adequacy will allow to observe this quality. In addition, the ANOVA Tables 3.1, 3.2 and 3.3 confirm the model's suitability graphics (check the coefficient R^2).

CONCLUSION

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

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. However, in choosing a treatment pathway, one must take into account both the normative objectives to be achieved and the cost of treatment.

To compare the results obtained with each coagulant, the color removal efficiency [9] was estimated taking into account the organic matter removal and color performance.

Aluminum sulfate produces less sludge for a given yield of COD or color.

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 characteristics of the raw effluent. 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.

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