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Optimization of a Physicochemical Pretreatment Combined with Biological Treatment for a Highly loaded Wastewater with Anionic Surfactants, Using Response Surface Methodology (RSM)

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Abstract: In the arid land, water resources are facing two major problems, the first is a quantitative one, which is their scarcity, and the second is qualitative, related to water pollution and contamination. Trying to solve these problems, suppose that water reuse can be a potential and strategic solution for these areas. This solution requires developing new methods and technologies for the treatment of polluted water. In Tunisia, anionic surfactants are very common pollutants found in water, coming mainly from detergent and cosmetic industries as well as daily uses such as washing and cleaning. Biological treatment using membrane bioreactor (MBR) has shown very good performance for the treatment of this kind of pollutants, but it becomes insufficient at high concentrations, which cause harmful effects on the reactor biomass. In this work, we tried to optimize a new method for the treatment of an industrial wastewater, highly loaded with anionic surfactants (about 4 g/l), especially Linear Alkyl Sulfonate (LAS), coming from a cosmetic industry in Sfax city in Tunisia. This method combines a physicochemical pretreatment by coagulation-flocculation using lime and alumina sulfate, with a biological treatment using MBR. The optimization was carried out using Response Surface Methodology (RSM) through a two factors central composite plan, to adopt the physicochemical pretreatment conditions for the smooth functioning of the whole process, in order to obtain treated wastewater that fit the Tunisian standard NT 106.02 to be released in aquatic environment. As results, the integration and optimization of the physicochemical pretreatment have allowed to decrease the anionic surfactants concentration by 43 %, the Chemical Oxygen Demand (COD) by 48% and the suspended matter (clogging factor) by 87.5%, making the MBR operating properly and releasing treated wastewater that respect the standards specified by law.

Key Words: Anionic surfactants, Coagulation-flocculation, RSM, Wastewater

1. Introduction

In the arid and the semi-arid region, countries like Tunisia are facing increasingly more serious water shortage problems. Problems of water scarcity will intensify because of population growth, rise in living standards, and accelerated urbanization which threaten the water supply in general and lead to both an increase in water consumption and pollution of water resources (Maelet and Ruelle, 2002). Continuing increase in demand by the urban sector has led to increased utilization of fresh water for domestic purposes, on the one hand, and production of greater volumes of wastewater on the other. One way to cope with these problems is to reuse wastewater. This solution requires developing new methods and technologies for the treatment of polluted water.

In Tunisia, anionic surfactants are very common pollutants found in water, with more than 100000 m^3/year of surfactant containing wastewater released, coming mainly from detergent and cosmetic industries as well as daily uses such as washing and cleaning. MBR technology has shown very good performance for the treatment of this kind of pollutants (Dhouib *et al.*, 2005). But this method is confronted to some limits in high concentration of AS, due to their toxicity toward microorganisms and foaming in aerated bioreactors, on the hand, and high COD and Total Suspended Solids (TSS) which accelerate the clogging of the membrane of the bioreactor, in the other hand; which made the idea of integrating a physico-chemical pretreatment, interesting to overcome these limits.

In this work, we tried to optimize a new method for the treatment of an industrial wastewater, highly loaded with anionic surfactants (about 4 g/l), especially Linear Alkyl Sulfonate (LAS), coming from a cosmetic industry in Sfax city in Tunisia. This method combines a physicochemical pretreatment by coagulation-flocculation using lime and alumina sulfate, with a biological treatment using MBR. The optimization was performed on the operational parameters of the new physicochemical pretreatment to reduce the COD and the anionic surfactant amount (AS) by, at least, 30% and 25%

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Table 1. Wastewater main characteristics.

Characteristic	Mean value	Standard deviation
pH	5.56	0.32
COD (g/l)	18.250	3.112
BOD (g/l)	1.211	0.125
TSS (g/l)	2.230	0.950
AS (g/l)	3.900	0.520
N_t (g/l)	0.155	0.012

respectively, in order to allow the good operating of the MBR, and thus, the release of an outlet that fit the standard NT106.02.

2. Materials and Methods

2.1. Industrial wastewater

The wastewater was collected from the equalization tank of wastewater treatment plant of a cosmetic company (HENKEL, Sfax, Tunisia) during the optimization, characterized and stored at 4˚C. The characteristics are shown on **Table 1**.

2.4. Analytical techniques

- pH was analyzed using a Metrohm pH-meter.
- Methylene Blue Active Substance (MBAS) assay used to the estimation of anionic surfactants. This assay was carried out according to Tunisian Norms NT 01-28 (1983). As well, Hyamine colorimetric method was also used for estimating the anionic surfactants in wastewater when concentrations exceed 40 mgL^{-1}.
- COD was estimated as described by Knechtel (1978).
- Total suspended solids (TSS) were measured as mentioned in the standard methods for examination of water and wastewater (American Public Health Association / American Water Works Association / Water Environment Federation, 1992).

2.2. Coagulation-flocculation

Flocculation and coagulation are mainly used, when the application of sedimentation is not feasible, due to the presence of extremely fine particles or globules, which do not possess a significant settling rate, because the phases do not appreciably differ in density from the parent liquid (Zouboulis and Avranas, 2000).

The experiments were carried out at laboratory bench scale using a jar test apparatus “Numerical Flocculator 10408, Fisher Bioblock Scientific” with alumina sulfate and lime as described by Aloui *et al.* (2009).

2.3. Experimental design

The central composite design (CCD), which is the standard

Table 2.Correspondence between coded levels and real values.

Coded levels (x_i)	-1.4142	-1	0	1	1.4142
pH (X_1)	6.79	7.00	7.50	8.00	8.21
Coagulant d. (X_2)	0.944	1.400	2.500	3.600	4.056

Table 3. Central composite design and responses results.

Run No.	Coded X_1	Coded X_2	Y_1	Y_2
1	-1	-1	8.87	24.49
2	1	-1	12.51	4.08
3	-1	1	33.49	44.90
4	1	1	16.75	16.33
5	-1.4142	0	24.63	18.37
6	1.4142	0	25.12	6.21
7	0	-1.4142	19.92	2.04
8	0	1.4142	54.76	42.86
9	0	0	23.56	8.16
10	0	0	24.08	6.12
11	0	0	34.48	8.16
12	0	0	28.10	6.12
13	0	0	24.68	4.08
14	0	0	16.47	3.04
15	0	0	23.43	3.04
16	0	0	26.61	4.16
17	-0.6124	-0.3536	27.67	6.12
18	0.6124	-0.3536	18.95	2.04
19	0	0.7071	33.36	18.37

RSM, was selected to optimize two most effective operating variables in the coagulation–flocculation process, namely the coagulant dosage and pH. For statistical calculations, the variables X_i were coded as x_i according to the following equation:

$$x_i = \frac{X_i - X_0}{\delta X} \qquad (1)$$

Where X_i is the uncoded value of the *i*th independent variable, X_0 the value of X_i at the centre point of the investigated area and δX is the step change.

The range and levels of pH (X_1) and Coagulant dosage (X_2) are given in **Table 2**.

The two responses measured, COD removal (Y_1) and AS removal (Y_2), were calculated in %, and the response variables were fitted by a second-order model in the form of quadratic polynomial equation:

$$Y_m = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{i<j}\sum_{j} b_{ij} X_i X_j \qquad (2)$$

Where Y_m is the response variable to be modeled; X_i and X_j the independent variables which influence Y_m; b_0 , b_i , b_{ii} and b_{ij} are the offset terms, the *i*th linear coefficient, the quadratic

Table 4. ANOVA table for COD removal.

Source of variance	Degrees of freedom	Sumsof squares	Mean squares	F-statistic	p-value
Regression	1.11111E+003	5	2.22221E+002	3.8240	0.0238
Residues	7.55453E+002	13	5.81118E+001		
Validity	1.76267E+002	6	7.93778E+001	5.1488	0.0246
Error	1.07918E+002	7	1.54169E+001		
Total	1.86656E+003	18			

coefficient and the *ij*th interaction coefficient, respectively.

Model terms were selected or rejected based on the P value (probability) with 95% confidence level. Three additional experiments were conducted to verify the validity of the statistical experimental models (test points method) (Run No. 17, 18 and 19 in **Table 3**).

3. Results and Discussion

3.1. Modeling of COD removal (Y_1)

The COD removal values of the coagulation–flocculation experiments are listed in Table 3. The following equation is a regression model with the experimental results:

$$Y_1 = 24.547 - 0.974X_1 + 9.557X_2 - 2.966X_1^2 + 3.119X_2^2 - 5.503X_1X_2 \quad (3)$$

Statistical testing of the model was performed with the Fisher's statistical test for analysis of variance (ANOVA) (**Table 4**). The quadratic regression shows that the model was significant and the p-value (0.0238) implies that the second-order polynomial model fitted the experimental results well. The contour plots of Y_1 (**Fig. 1**.a), obtained from the model, show that the latter has an hyperbolic shape describing the double effects of the factors interaction. The COD removal surface, presented in Figure 1.b, give an idea about the coordinate of the desired COD removal percentage, serving for the multiple responses optimization.

3.2. Modeling of AS removal (Y_2)

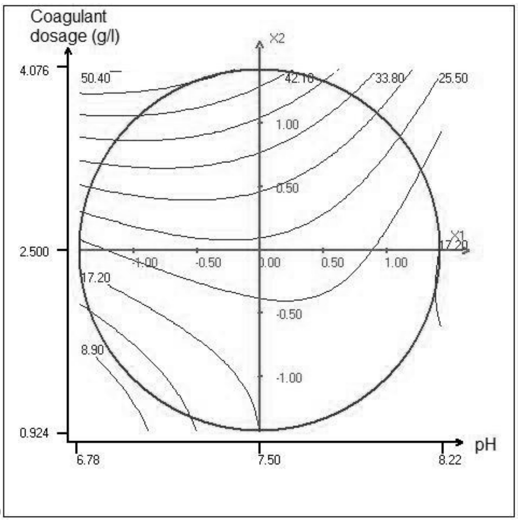
The following model was obtained from the analysis of AS removal results shown in Table 3:

$$Y_2 = 5.533 - 7.373X_1 + 11.330X_2 + 4.608X_1^2 + 9.732X_2^2 - 2.687X_1X_2 \quad (4)$$

The ANOVA analysis (**Table 5**) shows that the model was significantly valid (p-value<0.001).

The contour plots (**Fig. 2**.a) show that the AS removal model has an elliptic shape proving existing interactions between factors effects, these plots have allowed to draw the corresponding response surface (Fig. 2.b), showing different response levels ranging from non significant removal, about 0.5 to more than 48%.

(a)



(b)

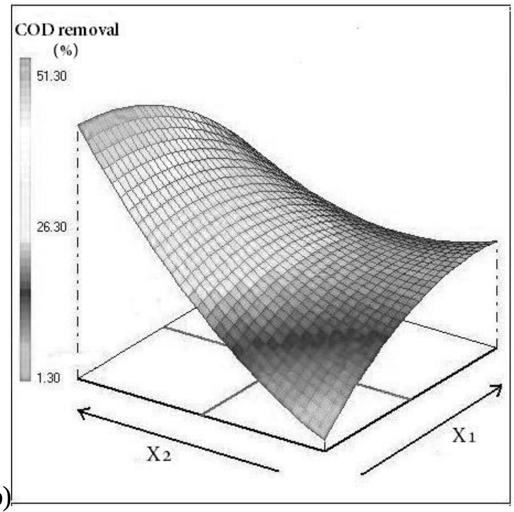


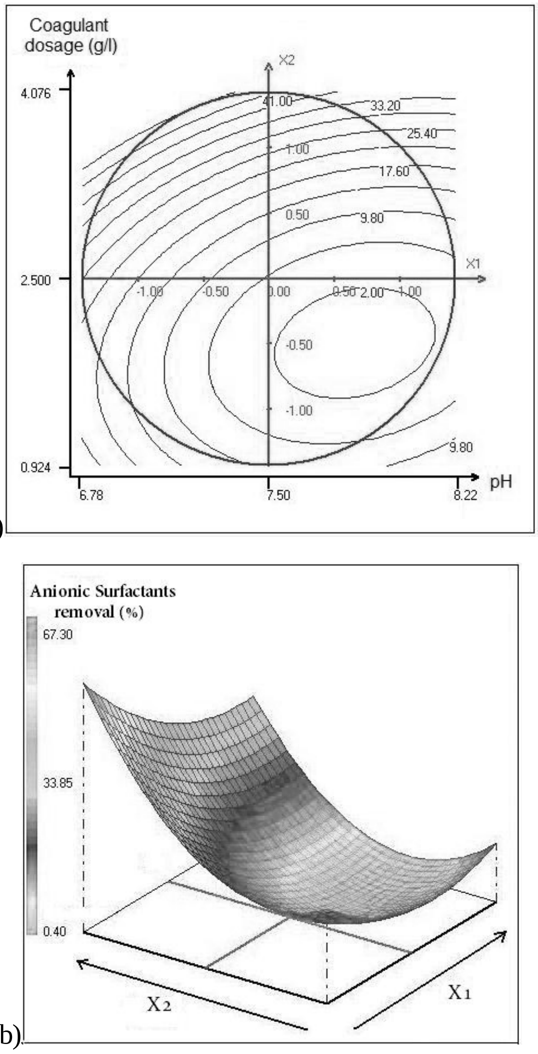
Fig. 1. Contour plots (a) and surface graph (b) for COD removal.

Table 5. ANOVA table for AS removal.

Source of variance	Degrees of freedom	Sumsof squares	Mean squares	F-statistic	p-value
Regression	2.61125E+003	5	5.22249E+002	76.3867	<0.001
Residues	3.83844E+002	13	5.95265E+001		
Validity	3.35986E+002	6	5.59976E+001	8.1905	0.0069
Error	4.78584E+001	7	6.83691E+000		
Total	2.99509E+003	18			

3.3. Multiple responses optimization

As shown in the contour plots, the two responses have two different behavior in the experimental range, hyperbolic for the COD removal and elliptic for the AS removal, and the optimal conditions for the two responses cannot match. Therefore, to obtain a common optimum for the two responses at the same time, we chose to use the desirability functions.



(a) (b)

Fig. 2. Contour plots (a) and surface graph (b) for AS removal.

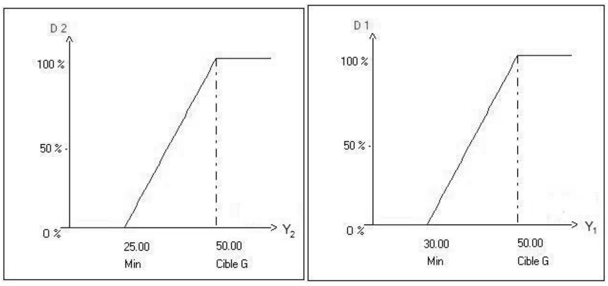


Fig. 3. Partial desirability functions : D_2 for AS removal(left) and D_1 for COD removal (right).

The partial desirability functions D_1 (for COD removal) and D_2 (for AS removal) were set as follow (**Fig. 3**.): For D_1 satisfaction start from at least 30% of removal which is required for the MBR smooth functioning, and achieves 100% for 50% of removal, which allow a good operating even with an unexpected increase of pollution loads.

The same for D_2, except the satisfaction start from 25% for the same reason.

Table 6. Industrial trials results by treatment step.

Treatment Steps	COD (g/l)	AS (g/l)	pH	TSS (g/l)
Raw wastewater	19.752	4.120	5.96	3.200
Standard deviation	0.614	0.280	0.37	0.720
Pretreated ww.	11.630	2.730	7.10	0.410
Standard deviation	0.440		0.04	0.072
Inside bioreactor	3.257	0.184	6.98	8.6
Standard deviation	0.216	0.022	0.16	0.56
MBR outlet	0.824	Not detect.	7.03	Not detect.
Standard deviation	0.073	----	0.14	----
Standard NT106.02	1.000	0.005	6.50-9.00	0.400

$$D = \left(D_1 * D_2\right)^{1/2} \qquad (5)$$

The global desirability function (Eq. (5))was maximized and we obtained an optimal global desirability of 85.57% with 83.7% for D_1 and 87.48% for D_2. This optimum correspond to coded pH level of -0.7328, and coded coagulant dosage of 1.2819, which match with the real values: pH of 7.02 and coagulant dosage of 4.011g/l.

3.4. Industrial trials of the whole optimized process

The optimized conditions were applied on the industrial process, and the results in **Table 6** were obtained from several trials and compared to the Tunisian standards.We note that the outlet of the whole process fit the standard in the AS concentration allowed, as well as in the other parameters.

4. Conclusion

The integration and the optimization of the physicochemical pretreatment has allowed the good operating of the treatment process and the release of a treated surfactant containing wastewater that fit the standards specified by Tunisian law.

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