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Effectiveness of a physicochemical coagulation/flocculation process for the pretreatment of polluted water containing Hydron Blue Dye

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ABSTRACT

In this work, the effectiveness and applicability of a physicochemical coagulation/flocculation process for the pretreatment of textile industry discharges containing Hydron Blue Dye using $Al_2(SO_4)_3$ as destabilizing agent was studied. The coagulation/flocculation performance on the quality of treated water was measured by UV absorbance at different wavelengths, by scanning electron microscopy and Fourier transform infrared spectroscopy. Results showed that the process was effective with a maximum yield of 77% under optimized conditions of pH, coagulant dosage, concentration of initial solutions, and stirring speed. The optimization of this process by a design of experiments allowed us to construct models with an R^2 value of 0.99 for the coagulation/flocculation in the chosen field.

Keywords: Coagulation/flocculation; Hydron Blue; Azoic dye; Experimental design

1. Introduction

The textile industry is one of the most polluting industries, producing high quantities of wastewater containing a large variety of chemicals. In fact, the world production of textile dyes is estimated to be over 10.000 tons per year and approximately 100 tones/year of dyes are discharged into wastewater [1]. The problem is even more serious in the case of industrial effluents, which have toxic nature. The presence of dyes leads to colored wastewater even at very low concentrations, which produces toxicological and technical problems and environmental pollution. Moreover, anionic dyes are highly soluble in water and have reactive groups which are able to form covalent bonds between dye and fiber [2].

Of late, increased public concern and strict environmental regulation have forced industries to pretreat effluents before discharging and to look for

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more efficient and economically viable options to treat these effluents. It has been observed that a limited number of dyes can be microbiologically degraded under anaerobic conditions, which in most cases leads to the generation of carcinogenic compounds [3,4]. In addition to this effect, most dyes are toxic, carcinogenic, mutagenic, or teratogenic themselves for various microbiological and fish species [5]. As an example, crystal violet [6], malachite green [7], and aniline blue are reported to cause cancer of aquatic organisms and are also mutagen and mitotic [8,9].

The most common processes used for the removal of dyes from wastewater are the following: adsorption, precipitation, electrocoagulation/electroflotation, reverse osmosis, membrane filtration, ion exchange, and chemical oxidation [10–12].

Adsorption technology is among the most effective but at low concentrations of pollutants; while at medium or high loads, efficiency decreases significantly since the adsorbent is saturated quickly. The usefulness of using another technique such as coagulation/flocculation pretreatment method could be efficient.

An increasing interest has focused on the development of different methods capable of removing these dangerous compounds from wastewater, consisting of hybrid processes resulting from various combinations of physical, chemical, and biological techniques.

The objective of this paper was to study the effectiveness and applicability of a physicochemical coagulation/flocculation process as a pretreatment of textile water containing dyes. The influence of the pollutant concentration, the amount of the coagulant $Al_2(SO_4)_3$, and the pH-solution on the quality of the process was investigated using the full factorial design and modeling the effects of these parameters on the kinetic constant. The approach involved two main steps: the first step concerned the kinetic study of the effect of the solution concentration, dosage of the coagulant, and the pH-solution; the second step was based on the use of full factorial design plans, with determining levels of factors to be tested. Graphs of the effects of factors will assess the effects of various parameters on process performance. The choice of a method for the wastewater treatment of a specific pollutant/dye will depend on a number of factors, following being the most significant: effluent composition, type of reuse, quality requirements, and installation size.

2. Materials and methods

2.1. Materials

The dye used in this study is Hydron Blue (Cassela©, Germany), Solutions were prepared by dissolving the required amounts of dye in distilled water. This approach consisted of preparing a mother solution with given concentration avoiding contact with sunlight. The chemical characteristics of this dye are given in Table 1.

Aluminum sulfate powder 18 times hydrated ($Al_2(SO_4)_3{\cdot}18H_2O$) with a molecular mass of 666 g mol^{-1} and a purity between 95 and 100% was purchased from PANREAC (France). A mother solution of 5 g/L was prepared periodically by dissolution in distilled water.

The chemical compounds used in this study (Table 2) are of analytical grade. All solutions were prepared with deionized water.

2.2. Methods

Experiments were performed in a wise Stir Jar tester composed of six beakers of 1 L. Each one has an arm with a blade capable of generating a maximum speed of 300 rpm and equipped with a lamp at the bottom allowing visualizing formed flocks. All experiments were performed at room temperature. Solutions to be treated were prepared at different concentrations of dye by diluting with distilled water.

pH was adjusted with 1 N of sodium hydroxide solution (1 N NaOH) and 1 N sulfuric acid solution (1 N H_2SO_4).

First, the beakers were placed on the flocculation ramp at 3/4 of their depths. $Al_2(SO_4)_3$ was added simultaneously at different concentrations and mixed at 200 rpm for 30 s. To obtain bigger flocks and easily settable mixtures, samples are then mixed over a period of 40–60 min ranging the rotational velocity of the blades from 40 to 150 rpm.

Samples were taken 30 s after the addition of the coagulant, then every minute during a period of 10 min, and every 5 min for a period of 60 min.

Collected samples were filtered using a filter paper no. 5 (0.45 μm) and the recovered flocks were characterized.

Filtered solutions were analyzed by spectrophotometer by UV with a spectrophotometer SCHIMADZU length, UV–vis mini 1240 CE. The optimum wavelength was obtained corresponding to their maximum absorbance scanning of the samples at a wavelength ranging from 190 to 800 nm. The spectrum obtained at an initial concentration of 50 mg/L of HB is shown in Fig. 1 with an optimal wavelength of 620 nm.

3. Results and discussion

3.1. Influence of the coagulant dosage

Determination study of coagulation/flocculation and the influence of some physicochemical parameters

Table 1
Chemical characteristics of HB dye

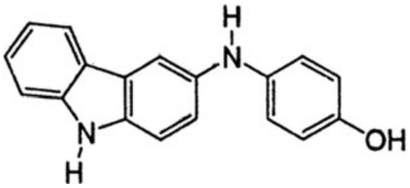
Chemical name	3-(4-Hydroxyanilino)carbazole
Name	Hydron Blue C.I. Vat Blue 43, C.I. 53630
Abbreviation	HB
Structure	
Chemical class	Carbazole class
λ_{max} (nm)	620
Molecular formula	$C_{18}H_{14}N_2O$
Molecular weight	274.32
CAS registry number	1327-79-3

Table 2
Experimental field for the study of dye vanishing

Coded experimental variables (X_i)	Factors (U_i)	Unity	Lower level	Higher level
X_1	U_1: time	min	10	40
X_2	U_2: C_{dye}	mg/l	1.0	5.0
X_3	U_3: $C_{Coagulant}$	mg/l	0.25	1.5
X_4	U_4: stirring speed	rpm	40	60

on them are very important for the optimization of certain processes at the industrial scale. The study of kinetics for the coagulation/flocculation process of dyes according to the coagulant dosage and the stirring speed of the initial concentration was performed.

As shown in Fig. 1, the addition of sulfate associated with the different steps of the coagulation/flocculation and sedimentation processes produces flocks which may contain a part of the sulfate present in the effluent treated.

To study the influence of the coagulant dosage on the HB disposal rate, the tests were performed on colored solutions with the following coagulant dosages: 0, 2.5, 5, 10, 15, and 20 mg/L, according to levels found in the literature [13,14]. The dye content was fixed at 5 mg/L for a reaction volume of 1,000 mL and an initial pH of 7.5. The obtained results are shown in Fig. 2(a).

In this graph are plotted the data corresponding to samples after 30 min of treatment. Since is the time commonly used in industry (from 20 to 30 min). The data were plotted as a function of the coagulant charge used (Fig. 2(b)). An optimum can be clearly observed at this graph.

As it is known, the metal cations of aluminum salts solutions create bonds with six surrounding water molecules. The strength of these bonds weakens the O–H bonds of water molecule; as a result, the H^+ ion is relegated into the solution and creates a hydroxide group which reduces the charge of the metal cation. This process of dissociation of water molecules is known as hydrolysis. It is important to mention that the appearance of H^+ necessarily causes a drop in pH (4.5 in our case) and alkalinity consumption. The rate of the hydrolysis reaction and the nature of formed species depend strongly on the concentration of aluminum salts in solution and their pH. The hydrolysis products contain cationic monomers, complex cationic polymers, microcrystals, and a precipitate of the hydroxide of the metal ion.

At low concentrations and favorable pH conditions, coagulation by aluminum salts is achieved by neutralization of surface charges of the particles in suspension. Soluble cationic monomers generated by the hydrolysis are adsorbed on the surface of particles (mineral and organic) of opposite sign causing neutralization of surface charges. The adsorption of these hydrolysis products is higher than that of the metal

Fig. 1. The dye before and after treatment.

ion (Al^{3+}). Under such conditions, we find in suspension soluble cationic monomers and cationic hydroxide precipitates which are actively involved in the coagulation/flocculation phase. These two species, therefore, participate in the neutralization of surface charges of suspended particles according to a model called "Precipitation Charge Neutralization". This method of coagulation is characterized by the existence of an optimum dosage of coagulant called critical concentration of coagulation (CCC), which will be determined in this study. Adding excess coagulant led to an inversion of surface charges of the particles, which become positive.

It was observed that there was high dye elimination at an HB concentration of 5 mg/l for using $Al_2(SO_4)_3$ and leading after 60 min of exposure to a 64% reduction. Increasing the coagulant dosage from 5 to 20 mg/L decreases the rate of reduction slightly for the same initial dye concentration. This rate reaches the threshold value of the total abatement of 64%. It is due to the role of the coagulant at low doses which reacted on the colloidal dye molecules by destabilizing them and neutralizing negative charges.

In Fig. 3(b) are depicted the residual contents expressed relatively to the initial concentrations (C/C_0) vs. the coagulant concentration for a treatment time of 30 min. The usual coagulation/flocculation levels are observed.

Indeed, it can be seen at low coagulant concentration, i.e. less than 5 mg/L, an improvement of coagulation by gradual addition of positive charges leading to charge neutralization of the dye particles. The formed flocks during this phase beyond the optimal dosage present reduced volume and are very compact.

There was observed a profitability of particles little pronounced leading to a lower efficiency. During this step, the formed flocks have larger volumes but less compact. The sweep flow phenomenon is observed. This profitability of colloidal particles (in our case, dye particles) can be explained by the hypothesis of Desjardins [14], which assumes that the charges issued from the surplus of the coagulant are adsorbed to the particle surface. The particles, which became profitable, have an inverse charge which is contrary to the purpose search tasks.

The influence of stirring speed and stirring time upon the dye removal for the three dyes was studied. For this purpose, three series of experiments were carried out varying the stirring speed of the jar test blades from 20 to 160 rpm, according to values found in the literature [14]. The dye content was fixed at 5 mg/L for a reaction volume of 1,000 mL and an

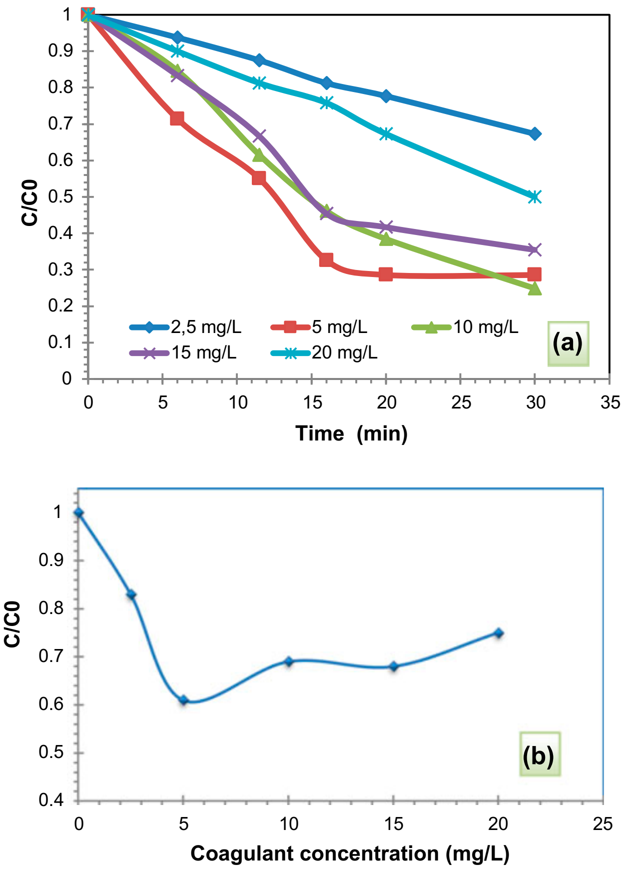


Fig. 2. (a) Influence of coagulant concentration on the dyes removal and (b) influence of coagulant concentration on the dye removal for a treatment duration of 30 min.

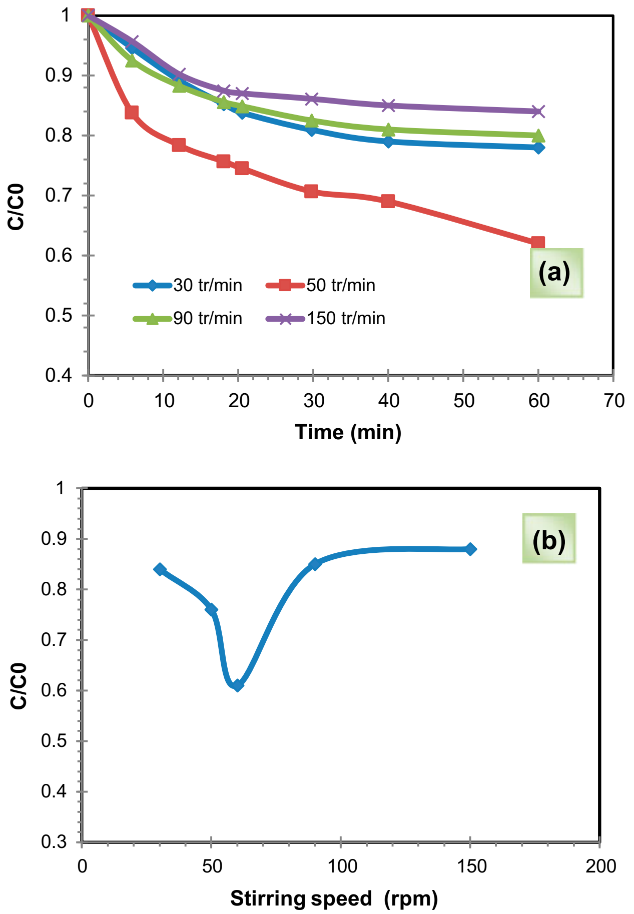


Fig. 3. Influence of stirring speed and stirring time (a) and influence of the stirring speed on residual concentration rate (expressed as C/C_0) in the case of coagulation/flocculation of colored solutions (b).

initial pH of 7.5. The obtained results are shown in Fig. 3(a) for the Hydron Blue (HB). Data corresponding to a treatment time of 30 min are plotted in Fig. 3(b).

We obtained the best yields of discoloration for a speed of 60 rpm for HB dye. These relatively slow speeds reduce the dissipated mechanical energy and, therefore, the velocity gradient imposed at the orthokinetic phase has an influence on the performance of the process.

Researchers normally fail to optimize this step because of the assumption that it would have a little influence on the removal of organic matter, which explains that there is a lack of interest by investigators to optimize the slow stirring parameters. Semmens and Ayers [15] concluded that no improvement is observed during removal of dissolved organic compounds by ferric sulfate flocculation. Furthermore, Lefebvre and Legube [16] have tested times of 10–30 min at a speed of 30 rpm and concluded that slow agitation step doesn't affect the dyes flocculation; then, a stirring time of 10 h is necessary.

The obtained results showed that the optimal speed is between 50 and 60 rpm promoting neutralization of particles with a negative charge, which lead to the formation of the flocks.

An aggregation of destabilized particles by charge neutralization is a slow process, especially for low concentration suspensions. Indeed, although this mechanism increases the efficiency of collisions, it is of no influence on their frequency, thus on aggregation rate. Practically, the stakes of this mode of coagulation are based on the choice of scales of stirring speed during the destabilization of particles in suspension, on their degree of aggregation, on settling time for sufficient removal of destabilized particles, and on the choice of parameters and equipment for measuring and monitoring the coagulation.

From Fig. 4, it seems that regardless of the initial concentration of simple compounds and coagulant dosage, the removal efficiency of these compounds is low. However, results obtained do not allow identifying a stoichiometric relation between the coagulant and the initial dye concentration. Unlike simple compounds, efficiencies are very important and may exceed 80% at high dye concentrations.

We can also see that, for all levels of tested dye, there is always an optimal concentration of aluminum sulfate from which the elimination stabilizes. Note also that the monitoring of the pH flocculated solutions showed a progressive decrease with increasing the dosage of coagulant (pH generally ranging from 6.0 to 4.0). This was predictable by hydrolysis reactions of aluminum sulfate.

Coagulation by charge neutralization is then a slow and difficult-implemented process, which requires expensive means for monitoring water treatment. In practice, operators skip these disadvantages using high amounts of aluminum salts beyond the solubility of the amorphous hydroxides. Then, an intense precipitation of hydroxides occurs increasing the concentration of the suspension and consequently the aggregation speed. This process, by which suspended particles (in our case, the dye) adsorb hydroxide precipitated particles, is called "coagulation driving". It produces flocks larger and denser than those obtained by charge neutralizing.

The main advantage of this type of coagulation is its independence with respect to the nature of the particles in suspension. In this coagulation mode, the optimal dosage is the coagulant concentration, which gives faster hydroxide precipitation.

It can be seen that, regardless of the initial concentration of simple compounds and coagulant dosage, the removal efficiency of these compounds is low. It varies between 44 and 50% for HB. Therefore, the removal efficiencies seem to be influenced by the concentration of introduced coagulant.

Obtained results do not allow identifying a stoichiometric relation between the coagulant and the initial dye concentration. Unlike simple compounds, efficiencies are very important and may exceed 80% for high dye concentrations.

We can also see that, for all levels of tested dyes, there is always an optimal concentration of aluminum sulfate from which the elimination stabilizes.

The rate of degradation is a function of the pH solution. The results of these tests (Fig. 5) show that a better performance of the coagulation/flocculation is obtained in a basic medium of the solution (before the addition of the coagulant). Results are plotted in Fig. 5, noting that the pHs after addition of the coagulant are respectively equal to: 2, 2.5, 2.75, 3, 3.5, 4.5.

The interpretation of these results and eventually the acid–base character of the dye depend on the pH of the medium [17].

Since a coagulant with acidic pH (pH 2) was used in this study, the reaction medium will be acid and then the results are obtained in acidic pH, which can be explained by the fact that in acidic medium, the solution becomes positively charged and promotes the adsorption of dyes on the coagulant.

Obtained results in the current study confirmed the data previously reported by other authors concerning the removal of dyes for pH ranging generally between 3 and 7 depending on the nature of the coagulant (in our case, $Al_2(SO_4)_3$ [18]. It is important to point out that for the above pH, dyes are present in a neutral form. The removal of these compounds

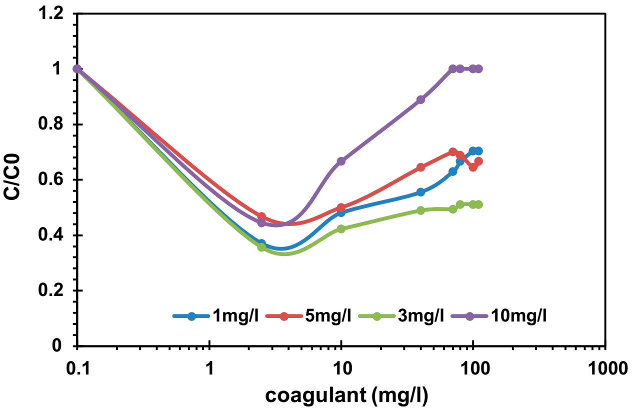


Fig. 4. Influence of coagulant dosage on the removal of different dyes concentrations.

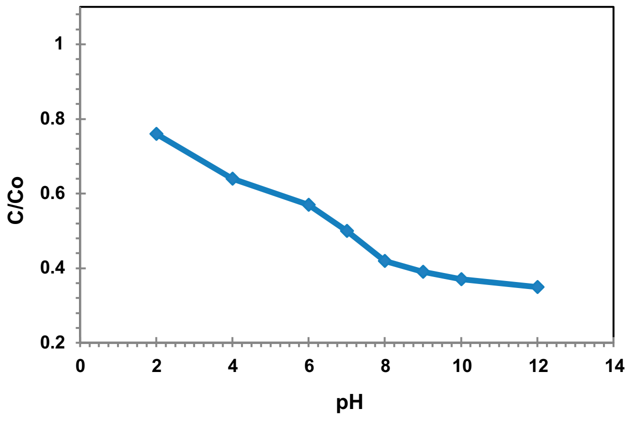


Fig. 5. Influence of pH solution on the residual concentration rate (expressed as C/C_0) in the case of coagulation/flocculation of colored solutions.

increases for pH 10. It is evident that their dissociated form would be much less attacked by flocculation with aluminum sulfate. The mechanisms involved in the coagulation of the dyes may be more complex because the pH also affects the chemical forms of aluminum and, therefore, the mechanisms involved in the removal of these compounds can be very different.

Table 3
Experience matrix, experience plan, and experimental results

Experience no.	Experience matrix				Experience plan				K
	X_1	X_2	X_3	X_4	U_1	U_2	U_3	U_4	
1	−1	−1	−1	−1	1	0.25	40	20	0.68
2	+1	−1	−1	−1	5	0.25	40	20	0.86
3	−1	+1	−1	−1	1	1.5	40	20	0.71
4	+1	+1	−1	−1	5	1.5	40	20	0.65
5	−1	−1	+1	−1	1	0.25	60	20	0.70
6	+1	−1	+1	−1	5	0.25	60	20	0.74
7	−1	+1	+1	−1	1	1.5	60	20	0.74
8	+1	+1	+1	−1	5	1.5	60	20	0.45
9	−1	−1	−1	+1	1	0.25	40	40	0.25
10	+1	−1	−1	+1	5	0.25	40	40	0.36
11	−1	+1	−1	−1	1	1.5	40	20	0.15
12	+1	+1	−1	+1	5	1.5	40	40	0.45
13	−1	−1	+1	+1	1	0.25	60	40	0.8
14	+1	−1	+1	+1	5	0.25	60	40	0.71
15	−1	+1	+1	+1	1	1.5	60	40	0.73
16	+1	+1	+1	+1	5	1.5	60	40	0.51
17	0	0	0	0	3	0.75	50	30	0.60
18	0	0	0	0	3	0.75	50	3	0.62

4. Effect of parameters on the kinetic of coagulation

The influence of four factors on the kinetic of dye vanishing was studied: time (U_1), the concentration of coagulant (U_2), dye concentration (U_3), and time (U_4). We adopted the methodology of experimental research based on full factorial plans [19,20]:

$$\begin{aligned} Y = a_0 &+ a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_4 + a_{12} X_1 X_2 \\ &+ a_{13} X_1 X_3 + a_{14} X_1 X_4 + a_2 3\, X_2 X_3 + a_{24} X_2 X_4 \\ &+ a_{34} X_3 X_4 + a_{123} X_1 X_2 X_3 + a_{124} X_1 X_2 X_4 \\ &+ a_{134} X_1 X_3 X_4 + a_{234} X_2 X_3 X_4 + a_{1234} X_1 X_2 X_3 X_4 \end{aligned} \tag{1}$$

where Y is the experimental response; X_i are the coded variables (−1 or +1); b_i is the estimation of the main effect of factor i for the response Y; b_{ij} is the estimation of the effect of interaction between the factor i and the factor j for the Y response.

The studied response is the apparent kinetic constant (k_{app}) of the coagulation/flocculation reaction for the azoic dye. Results are summarized in Table 3. It can be observed that the coagulant dosage and the stirring speed play a crucial role in the results of the tests. It is also important to remark the effect of concentration on the reaction kinetics. A more precise analysis can confirm these initial findings.

Table 4
Analysis of coefficients and model coefficient

Coefficient	Value	Standard deviation	Statistic t	T_{crit} 2.132
Constant	0.6061111	0.00255	237.72	Significant
X_1	−0.014375	0.002704	−5.32	Significant
X_2	−0.031875	0.002704	−11.79	Significant
X_3	0.066875	0.002704	24.73	Significant
X_4	−0.085625	0.002704	−31.66	Significant
X_1X_2	−0.044375	0.002704	−16.41	Significant
X_1X_3	−0.055625	0.002704	−20.57	Significant
X_1X_4	0.001875	0.002704	0.69	Non-significant
X_2X_3	−0.033125	0.002704	−12.25	Significant
X_2X_4	0.021875	0.002704	8.09	Significant
X_3X_4	0.100625	0.002704	37.21	Significant
$X_1X_2X_3$	−0.013125	0.002704	−4.85	Significant
$X_1X_2X_4$	0.026875	0.002704	9.94	Significant
$X_1X_3X_4$	−0.009375	0.002704	−3.47	Significant
$X_2X_3X_4$	−0.024375	0.002704	−9.01	Significant
$X_1X_2X_3X_4$	−0.001875	0.002704	−0.69	Non-significant

Table 5
Regression analysis

Source	Sum of squares	DDL	Mean square	F_{observed}	F_{critic}
Bond	0.50188125	13	0.038606	445.6353	5.87
Residues	0.00034653	4	0.000087	Prob. > F < 0001	
Total	0.50222778	17			

Table 6
Residues

Exp	Y_{mesured}	$Y_{\text{calculated}}$	Residues (ε)
1	0.68	0.680486	−0.00049
2	0.86	0.860486	−0.00049
3	0.71	0.706736	0.003264
4	0.65	0.654236	−0.00424
5	0.70	0.696736	0.003264
6	0.74	0.744236	−0.00424
7	0.74	0.740486	−0.00049
8	0.45	0.450486	−0.00049
9	0.25	0.250486	−0.00049
10	0.36	0.360486	−0.00049
11	0.35	0.354236	−0.00424
12	0.45	0.446736	0.003264
13	0.80	0.804236	−0.00424
14	0.71	0.706736	0.003264
15	0.73	0.730486	−0.00049
16	0.51	0.510486	−0.00049
17	0.6	0.606111	−0.00611
18	0.62	0.606111	0.013889

Table 7
Characteristic quantities

R^2	0.99
R^2a	0.99
Q^2	0.96
Press	0.00694
Normed Press	0.19632

The coefficients associated with each variable in the model were obtained. The analysis of these results allows identifying factors that do not have a significant influence on the studied response and, therefore, can be neglected from our study.

The variance analysis evaluates the probability that the variances of evaluated terms to be significantly different from the residual variance. In this case, results are used to determine factors and interactions whose probabilities are below an arbitrary level set.

This analysis is important because with reduces the number of dimensions of the problem identifying the factors and interactions statistically significant on the observed response and then neglect the others.

The results of the analysis of coefficients are depicted in Table 4.

The contribution of each factor was determined using a statistical analysis of variance (ANOVA) and results obtained are shown in Table 5 where it can be seen that the four factors X_1, X_2, X_3, X_4 are significant at about 99%, approximately. There is just 1% risk to reject the hypothesis of equality with the residual variance.

The Fisher's test used in ANOVA is achieved by taking the residual variance as a reference. Its results depend on, thereby, the number of rejected factors that may be different depending on the model of calculating. The Fischer's test is checked ($F_{\text{obs}} > F_{\text{crit}}$). So, the hypothesis H_0 is accepted.

From the results obtained by JMP software, the equations of the model involving the relevance of each factor and influential interactions are thus written as:

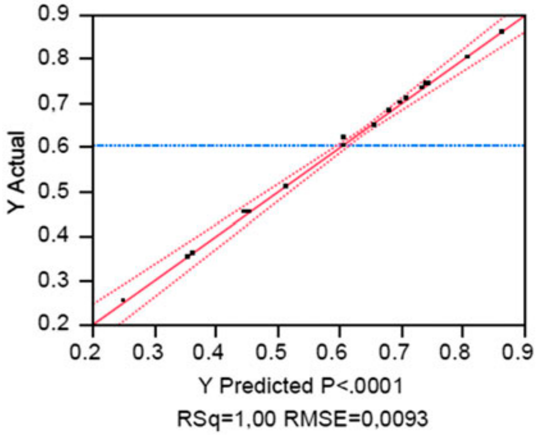


Fig. 6. Suitability graph of the model abatement rates interaction.

$$K = 0.60 - 0.014 \times X_1 - 0.031\,X_2 + 0.066 \times X_3 - 0.085 \times X_4 - 0.044 \times X_1 \times X_2 - 0.055 \times X_1 \times X_3 - 0.033 \times X_2 \times X_3 + 0.021 \times X_2 \times X_4 + 0.1\,X_3 \times X_4 - 0.013 \times X_1 \times X_2 \times X_3 + 0.026 \times X_1 \times X_2 \times X_4 - 0.0093\,X_1 \times X_3 \times X_4 - 0.0024 \times X_2 \times X_3 \times X4 \quad (2)$$

The crude analysis of residues (Table 6) provides no much information. However, it can be pointed out that there is a remarkable importance of residues on the experiences. The model is therefore corrected corresponding to the real function in the areas around these particular points.

The coefficient of determination R^2 and the adjusted R^2 are equal to (0.99, 0.99) for the dye (HB). Therefore, the mathematical model can be accepted as a satisfying model (Table 7).

It is possible to observe the descriptive quality with the suitability graph of the model shown in the Figs. 6 and 7. The point cloud is moderately aligned with the line $y = x$. The model is, therefore, descriptive enough. The classification of these factors and interactions in decreasing order about their effect on the efficiency is represented by the Pareto graph (Fig. 8).

The graphical analysis in this figure shows that the factor X_3 and X_4 have the most important effect on the kinetic constant because it has more than 50% of the response in the case of HB. Usually, the effect of a factor is represented by a line segment whose direction coefficient is the value of this effect.

Fig. 9 shows the interactions plot, showing a strong interaction between factors in the case of HB.

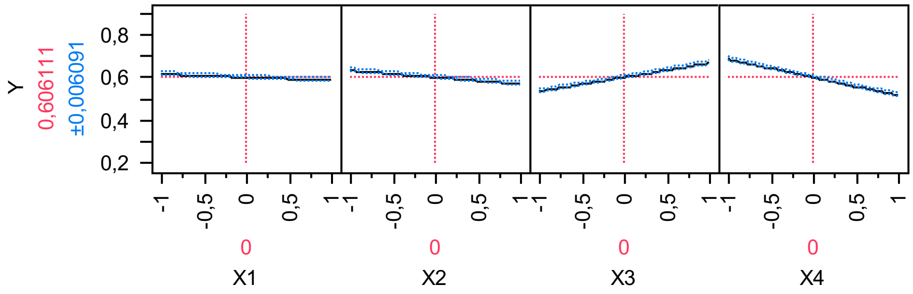


Fig. 7. Factor effect plotting.

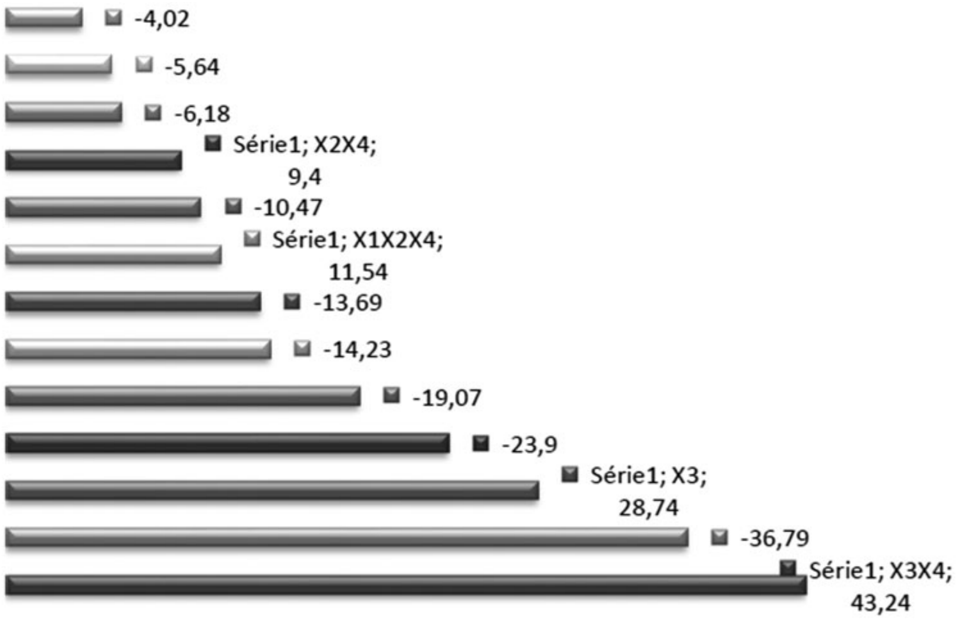


Fig. 8. Pareto diagram.

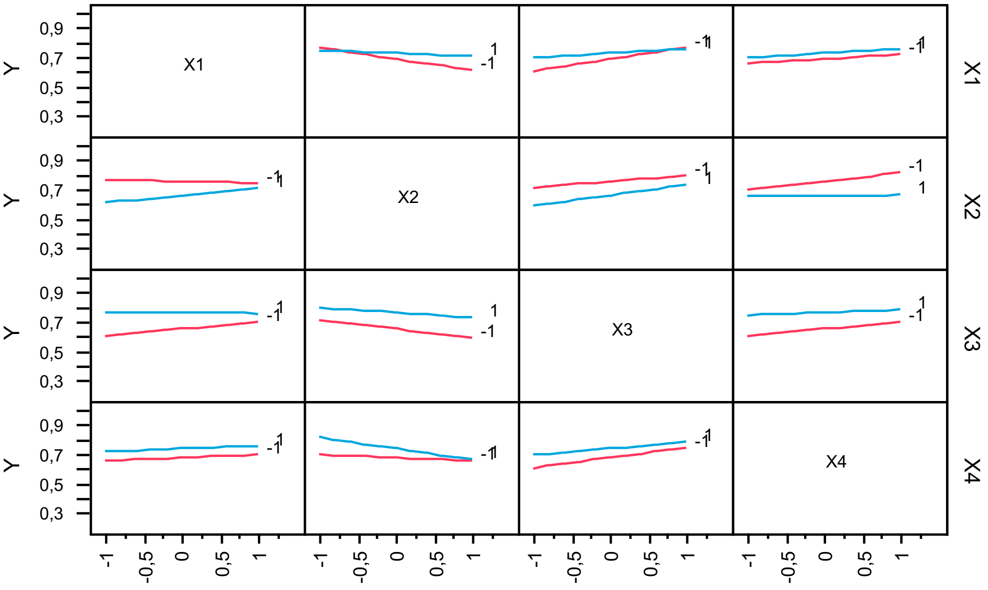


Fig. 9. Average interactions plotting.

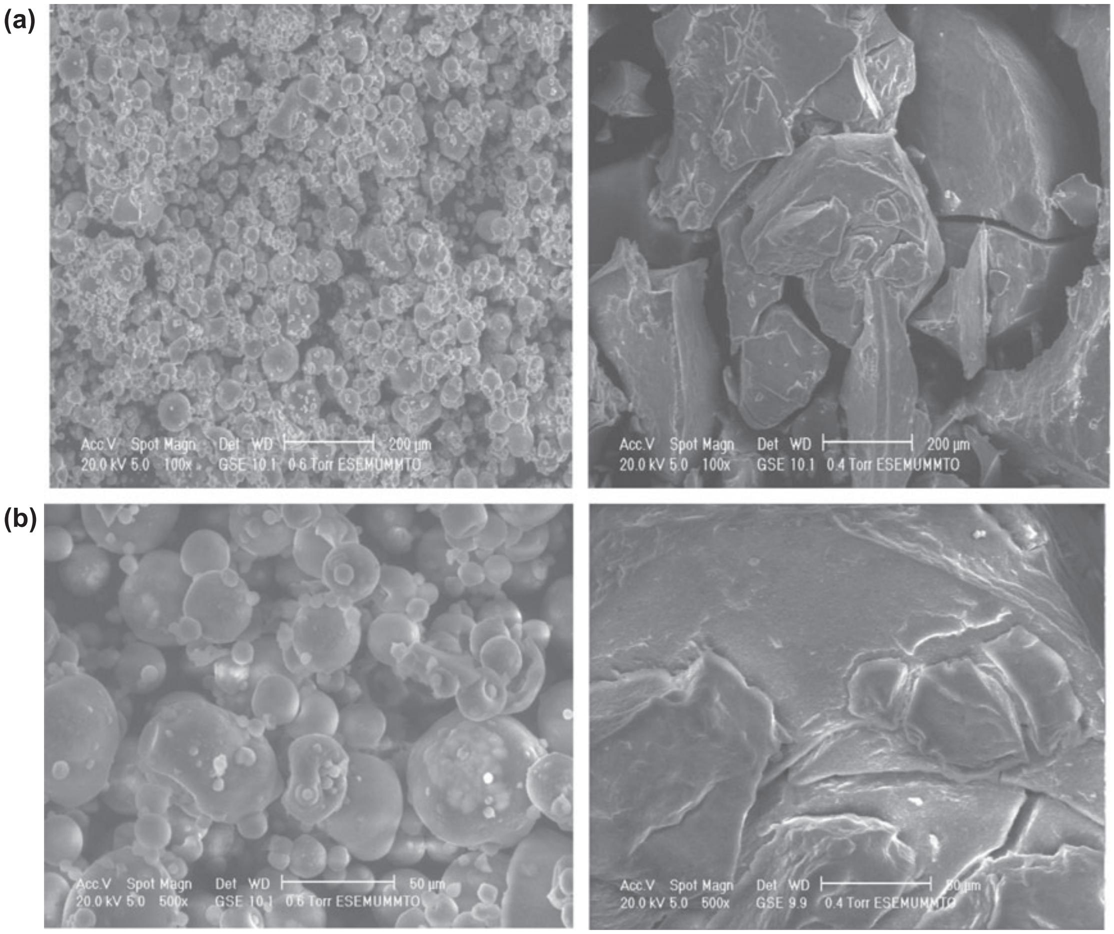


Fig. 10. SEM of HB dye before and after treatment: (a) at 200 μm scale and (b) at 50 μm scale.

5. Characterization of formed flocks

The scanning electron microscopy (SEM) gives information about the relief of the sample, the particle morphology, and their arrangement. The flocks were characterized by SEM in order to obtain maximum information about the surface state and homogeneity of the dyes before and after treatment.

Flocks were characterized by SEM before and after treatment in order to obtain the maximum information on the state of the surface and the homogeneity of the formed flocks. The images (Fig. 10) taken before treatment show fine and dispersed crystals, while the images taken after show the formation of homogeneous flocks, which explains the strong interaction between the dye molecules and the coagulant and confirms the irreversible capture of the pollutant which is an indication of the great efficiency of this removal process.

Characterization and qualitative study of the formed flocks were carried out by Fourier transform infrared spectroscopy (FTIR). Fig. 11(a) and (b) represents the FTIR spectra before and after dye treatment.

In the spectrum of the dye before the treatment, there is a presence of functional groups while there is the appearance of new areas in the corresponding spectrum after the treatment corresponding to func-

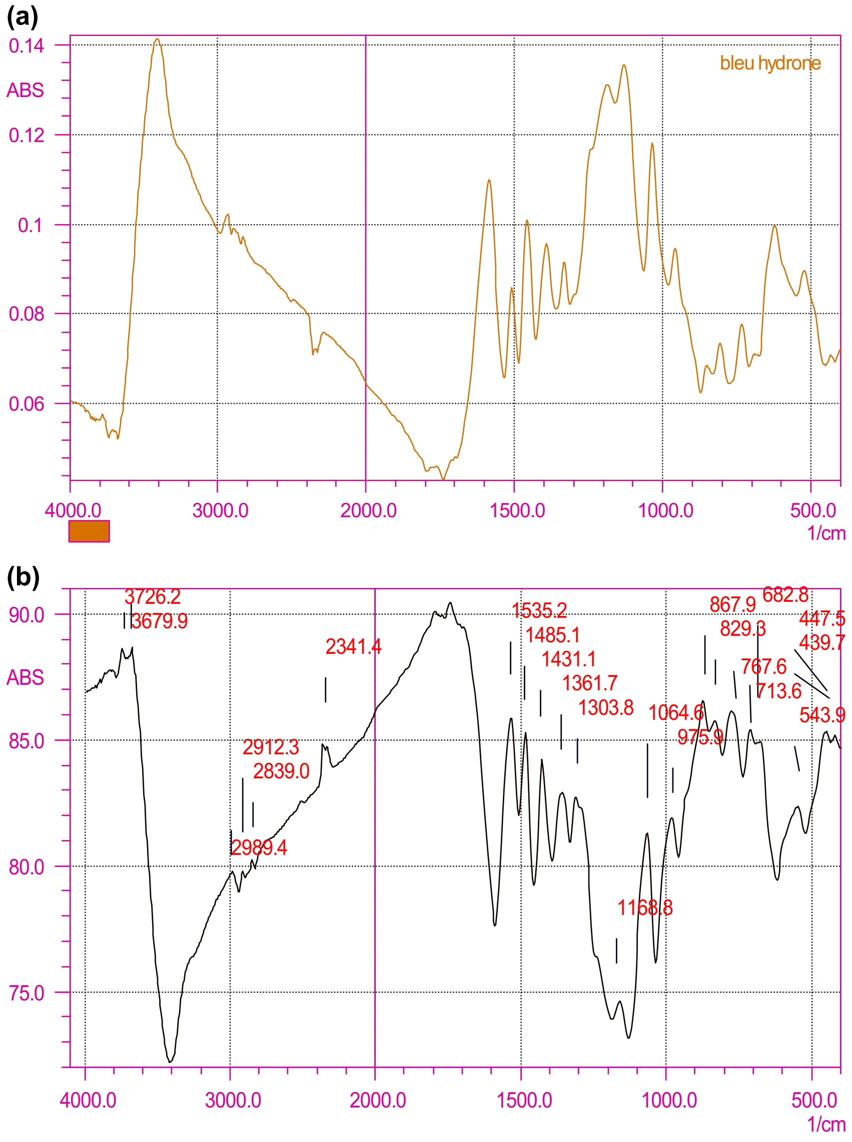


Fig. 11. FTIR spectrum of HB (a) before treatment and (b) after treatment.

tional groups of the coagulant. This result explains that the dye molecules are located inside the formed flocks, which coat them.

6. Conclusions

Relatively high removal rates were obtained, 64% for Hydron Blue (HB) in a short reaction time (20 min).

1. For all tested dye concentrations, there is an optimal dosage of the aluminum sulfate from which the removal is stabilized.
2. The rates are very high and can pass 80% for high dye concentrations and low coagulant concentrations.
3. Monitoring of the pH of flocculated solution shows that it decreases progressively with increasing coagulant dosage (pH varying in the 6,0–4,0 range), which was attributable through the hydrolyze reactions of aluminum sulfate.
4. Optimal stirring speeds vary between 50 and 60 rpm for the three dyes studied. The increase of the speed over 60 rpm is not favorable for the flocculation/coagulation since it generates the inverse phenomenon.
5. The characterization of the formed flocks by FTIR spectroscopy shows that all the characteristic bands of the different functions of the dyes and coagulant are present in the FTIR spectrum. It did not show that the dye was located inside the flocks indicating that the process was irreversible.
6. The analysis of formed flocks by SEM has revealed that all flocks have a homogenous structure.

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