Decolorization of BF Cibacete Blue (CB) and Red Solophenyle 3BL (RS) Using Aluminum Sulfate and Ferric Chloride

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Abstract: Coagulation process is largely applied for dye removal from textile wastewater treatment. This research aims to focus on implied mechanisms through coagulation of such wastewater. In this work, jar tests are performed to assess the coagulation process as a technique to treat synthetic solutions containing two textile dyes: BF cibacete blue (CB) and red solophenyle 3BL (RS). The effects of operational parameters such as coagulant type ($FeCl_3$ and $Al_2(SO_4)_3$. $18H_2O$ (alum)) and dose, initial pH, and dye concentration are studied. For a fixed 15 mg/L concentration of the two dyes, the $FeCl_3$ optimal doses are found to 80 and 20 mg/L for RS and CB with removal rates of 65 and 89%, respectively. Regarding alum, discoloration is achieved at 44 and 77% for CB and RS with optimal doses of 80 and 40 mg/L, respectively. Similar efficiency trends are also obtained for a 50 mg/L concentration of the two dyes. The involved coagulation mechanisms are: charge neutralization followed by precipitation of the insoluble dye-coagulant complexes, and their adsorption into the Al or Fe hydroxides. It would be interesting to follow a real effluent application on the textile industry possibly containing the two dyes tested in this work.

Keywords: Dye Decolorization, Coagulation, Ferric Chloride, Aluminum Sulfate, BF Cibacete Blue (CB), Red Solephenyle 3BL (RS)

1. Introduction

Dyeing wastewater contains great quantities of dyestuff together with important quantities of suspended matters, dispersing agents, salts and trace metals [1-6]. Dyeing wastewater can produce hard ecological issues because of its elevated color, big amount of suspended matters and elevated chemical oxygen demand [7]. Moreover, the composition of dyeing wastewater and textile industries changes considerably in a continuous manner, relying on the dyestuff, fabric and content of fixing chemicals which are injected. Unfixed dye ejects big doses of color to effluent. The dye is visible even at low levels. Therefore, treating this wastewater should satisfy not only the legal standards but also aesthetic standards [6].

Usual techniques of polluted water containing dyestuff comprise biological oxidation, chemical coagulation [8-16], advanced oxidation [17-20] and adsorption [6, 21, 22]. In a general manner, biological manners are frequently cheap and easy to use and are presently employed to eliminate organic compounds and color from dyeing and textile wastewater. Nevertheless, this dyeing polluted water cannot be easily break down chemically by classical biological techniques, such as the activated sludge manner, since the compositions of most commercial dye chemicals are usually very complicated and several dyes are non-biodegradable because

of their chemical tincture, molecular size; consequently, this generates sludge bulking. Even though dyestuffs and color matters in polluted water may be efficiently degraded using wet oxidation, advanced chemical oxidation such as H_2O_2/UV, O_3 and adsorption employing activated carbon, the costs of these techniques are relatively elevated [6].

Aluminum [23-28] and iron [29, 30] anodes have been employed for the electrochemical generation of hydroxide flocs that adsorb and eliminate metal-complex, disperse and acid dyes and other contaminants from the polluted water, which is identical to the mechanism of chemical coagulation [1-5, 8, 10, 18, 31 38].

Destabilization of colloids and suspended particles is frequently performed by modifying the solution pH degree or by injecting chemical reactants like ferric or aluminum salts combined with high molecular weight polymers of cationic, anionic or nonionic nature. [6]. Since most particles in natural waters are usually negatively charged (e.g., clays, humic acids [5, 35, 37], bacteria and dyes) in the neutral pH span (pH 6-8) [39], cationic coagulants are largely employed to attain particulate destabilization by charge neutralization [9]. Two main inorganic coagulants employed in water treatment [40, 41] are salts of aluminum and ferric ions. These hydrolysable cations are easily obtainable as sulfate or chloride salts in both liquid and solid type [42]. Nevertheless, ferric species are more insoluble than aluminum species and are also insoluble over a larger pH span. Therefore, ferric ions are usually selected to destabilize colloidal and suspended matters [6].

Included in the commercial textile dyes, disperse and reactive dyestuffs are of serious ecological worry due to their worldwide utilization. In order to contribute to the comprehension of dyes removal by coagulation process, we opted in this work to study the pH and coagulant dose effect. A great interest is accorded to the coagulation mechanisms for synthetic dyes removal. In this work, chemical coagulation was employed to eliminate two dyes: namely BF cibacete blue (CB) and red solopheny l 3BL (RS). The optimal coagulation parameters (i.e., pH and coagulant dose) were found out and the dye elimination performance of the two dye solutions was compared.
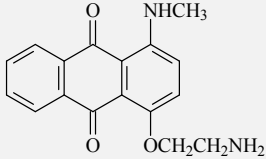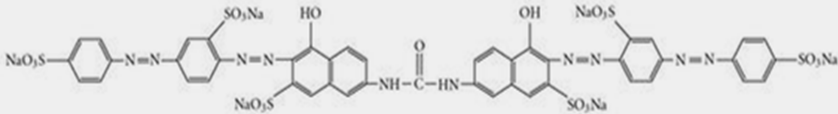
2. Materials and Methods

2.1. Dyes and Coagulant Solutions

2.1.1. Dyes Solutions

The two dyes used in this work are furnished by Boufarik Textile Manufactory (Algeria). Coagulation process experiments are performed for two dyes: namely BF cibacete blue (CB) and red solophenyl 3BL (RS). The main physicochemical properties of these dyes are shown in Table 1.

Table 1. Main characteristics of the studied dyes CB and RS.

Dye	Chemical structure	Molar mass (g/mol)	λ_{max} (nm)
CB	$C_{17}H_{16}N_2O_3$	296	635
RS	$C_{45}H_{26}N_{10}Na_6O_{21}$	1373	544

Quantities of the dyestuff powder are weighed and diluted in distilled water, in a volumetric flask, of volume relative to the concentration which it is desired to prepare. This preparation is followed by homogenization on a magnetic stirring plate, while avoiding contact with daylight (photochemical degradation of the dye). The used dye solutions (CB and RS) are prepared in dark bottles at initial concentrations of 15 and 50 mg/L, respectively.

2.1.2. Coagulant Solutions

In the jar test experiments, aluminum sulfate (alum), $Al_2(SO_4)_3 \cdot 18H_2O$, and ferric chloride, $FeCl_3 \cdot 6H_2O$ were used as coagulant reagents. Two synthetic solutions were prepared at a concentration of 1 g/L for both coagulants in 1 liter of distilled water by adding 1 g of the given coagulant. The prepared solutions must be well magnetically stirred until the coagulant will be completely dissolved. The stock solutions of 1 g/L are prepared periodically (before each test). All the used chemical products, such as HCl and NaOH, are of analytical grade.

2.2. Experimental Procedure

The jar test is a device that allows determining the optimal operating conditions of coagulation/flocculation process. The working mode of this device is according to the well-known general protocol of "jar test" on a coagulator/flocculator composed of six mechanical stirrers, of ISCO type (Figure 1), which are capable of generating the same speed.

Figure 1. Jar test device used in coagulation test experiments.

The experimental procedure for performing the jar test trials is summarized in Table 2.

Table 2. Technical procedure for performing the jar test trials.

Main steps for realizing the jar tests experiments	
Stage #1	During the tests; use a jar test device which is composed of six ramps.
Stage #2	Pour 500 mL of solution sample into each of the six beakers.
Stage #3	Place the beakers under the ramps of the device.
Stage #4	Set the contact times of the different treatment steps (coagulation-flocculation-decantation).
Stage #5	Measure the initial values of the main parameters: pH, visible absorbance and the temperature before the beginning of the test.
Stage #6	Start the rapid stirring at a speed of rotation of 150 rpm.
Stage #6	At time $t = 0$, add the coagulant doses as quickly as possible with a pipette and identically in each beaker. The doses are increasing so as to "frame" the presumed optimal injection.
Stage #7	Maintain the rapid stirring at the same speed of rotation of 150 rpm for 2 min.
Stage #8	Start the slow stirring program which is 40 rpm fixed for 20 min.
Stage #9	After 30 min of decantation, pipet the supernatant from each beaker.
Stage #10	The samples taken are filtered on a Millipore filter (0.45 μm in diameter). The filtrates are analyzed by UV-vis spectrophotometry to assess the effectiveness of the treatment.

2.3. Analytical Methods

The analytical method used in this study is UV-vis spectrophotometry for monitoring the discoloration of the aqueous dye solution. The spectrophotometric method requires, for its use, the establishment of calibration curve that relate the absorbance to the concentration of the sample to be analyzed.

The aqueous solutions of the dyes, CB and RS, studied, were prepared by respective dissolution of their powder in distilled water. This approach consists in first preparing a mother solution of given concentration. From this solution, we prepare, by successive dilutions, a series of solutions of well-defined concentrations (100, 80, 60, 40, 20 and 5 mg/L). The latter will then be analyzed by UV-visible spectrophotometry.

We thus establish the calibration line, representing the absorbance relative to the absorption maximum (λ_{max}), as a function of the concentration C (mg/L), thus obeying the Beer-Lambert law. This law is used to establish a relationship between the absorbance, the sample thickness and the concentration of the absorbing species. This relation is written:

$$A = \log \frac{I_0}{I} = \varepsilon \times C \times l \qquad (1)$$

with:

I$_0$: Intensity of the incident beam,

I: Intensity of the emergent beam,

A: Absorbance,

Ɛ: Specific extinction coefficient of the solute (10^3 cm^2 mg^1),

l: Thickness of the optical cell (l = 1 cm),

C: Solute concentration (mg/L).

The removal efficiency of the organic compounds is defined by:

$$R\ (\%) = \frac{(c_0 - c_f)}{c_0} \times 100 \qquad (2)$$

where C_o is the initial concentration of the organic compound and C_f its residual concentration at the end of the test.

The concentration C (mg/L) is deduced from the measurement of the absorbance (A) using a spectrophotometry and an optical path of $l = 1$ cm. Dosing of the dyes was carried out on a spectrophotometer of the

LOVIBOND type at the wavelength of λ_{max} = 635 and 544 for CB and RS, respectively.

2.4. Jar Test Experiments

In order to determine the effectiveness of the coagulation process, several tests were carried out by measuring the absorbance of the solutions before and after treatment. Two key parameters of coagulation are carefully examined, namely:

2.4.1. Effect of Coagulant dose

We varied the injection dose of added coagulant from 10 to 500 mg/L for the two dyes examined.

2.4.2. Effect of pH

In order to investigate the effect of pH on the coagulation of the two dyes treated with alum and ferric chloride, the pH is varied from 2 to 12. We adjusted the pH of the solutions using HCl and NaOH solutions (0.1 N).

All the experiments performed in this study were done three times to examine the reproducibility of the results.

3. Results and Discussion

This Section is devoted to the presentation of the results obtained after this experimental study of the coagulation of two organic dyes, BF cibacete blue (CB) and red solophenyle 3BL (RS) using alum and iron chloride.

3.1. Effect of the Coagulant dose

In order to study the effect of the coagulant dose (ferric chloride and alum) on the elimination of both CB and RS dyes, series of experiments were carried out at several doses of coagulants (10 to 500 mg/L) and at different initial concentrations of the two dyes. The results obtained, expressed in terms of percentage removal R (%) and plotted against the coagulant dose (mg/L), are shown in Figures 2 and 3 for both concentrations of dyes 15 and 50 mg/L, respectively.
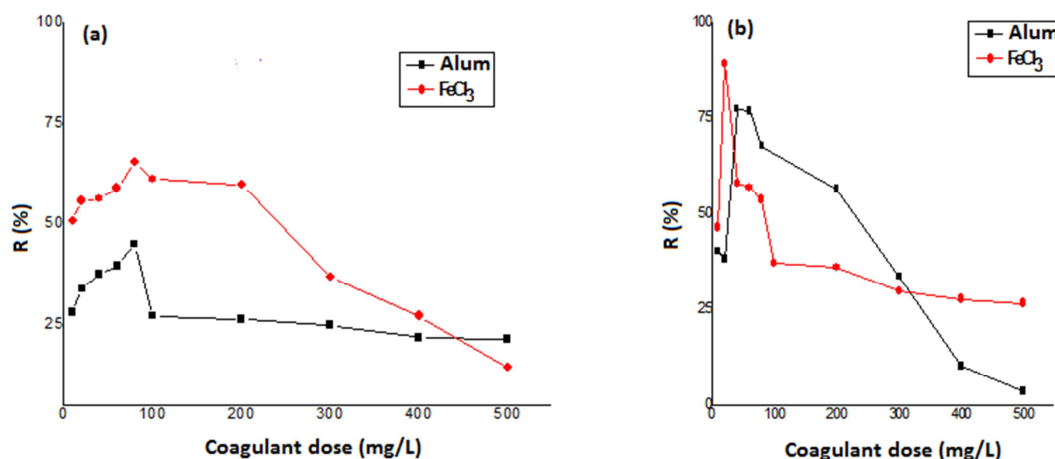

Figure 2. Effect of the dose of the two coagulants on the elimination of both dyes at 15 mg/L. (a) for CB, and (b) for RS.
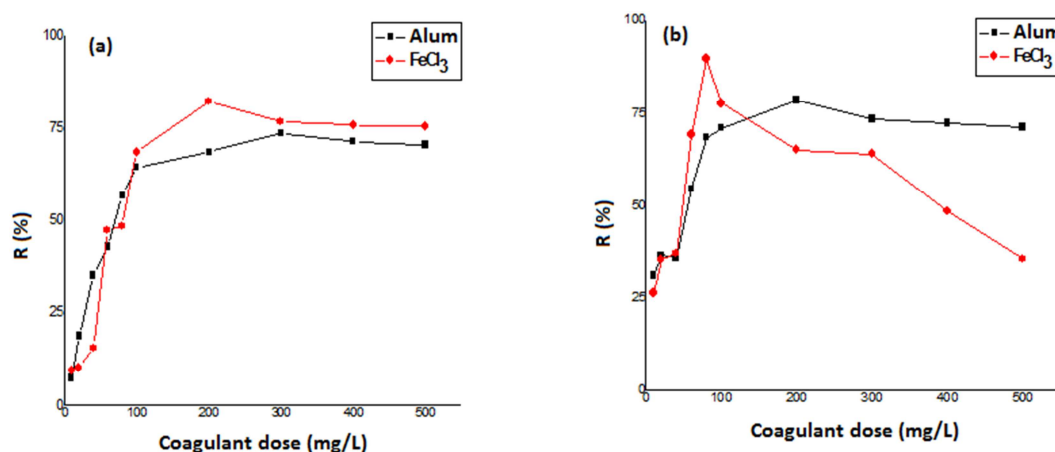

Figure 3. Effect of the dose of the two coagulants on the elimination of both dyes at 50 mg/L. (a) for CB, and (b) for RS.

We can see that with the increase in the coagulant dose, the rate of elimination increases to a certain value called optimal. By exceeding this optimum, there will be a gradual decrease in the yield *R* (%). We note that for a concentration of 15 mg/L (Figure 2) of the two dyes:

1) the optimal doses of FeCl$_3$ are of the order of 80 and 20 mg/L, for CB and RS with removal rates of the order of 65 and 89%, respectively.

2) For alum, a decolorization yield is reached at 44 and 77% for CB and RS at optimal doses of about 80 and 40 mg/L, respectively.

At concentrations of the two dyes of 50 mg/L (Figure 3), the results are summarized as follows:

1) For CB: $[FeCl_3] = 200$ mg/L, $R = 82\%$; [Alum] = 300 mg/L, $R = 73\%$.

2) For RS: $[FeCl_3] = 80$ mg/L, $R = 90\%$; [Alum] = 200 mg/L, $R = 78\%$.

By examining these results, we observe a poor performance of both coagulants at small doses. This suggests that the coagulant is insufficient to destabilize the dye molecules. At higher dosages exceeding the respective optima of the two coagulants tested, the reduction in color becomes less satisfactory than at the lowest dosages. This would indicate a kind of colloidal (or molecular) restabilization had occurred.

3.2. Effect of the Type of Coagulant

The results shown and discussed above put more emphasis on the well-proven performance of ferric chloride in the face of alum in terms of dye removal. This superiority in the efficacy of iron salt is well demonstrated in the literature [43].

In electrocoagulation process, as explained by Holt et al. [44], the size of the produced cation (10,000-30,000 nm for Fe^{3+} compared to 50-1,000 nm for Al^{3+}) was suggested to contribute to the higher efficiency of iron electrodes [36].

3.3. Effect of pH

There is no doubt that the initial pH of an organic solution in this case (or a suspension or surface water or even wastewater) is the main parameter of the performance of the coagulation process [45-47]. To study the impact of the initial pH on the elimination of dyes, we varied it in a wide range from 2 to 12 while keeping constant the two optimal doses of the coagulants. Figures 4 and 5 summarize the results obtained and show the evolution of the removal efficiency of each of the organic compounds tested as a function of pH.
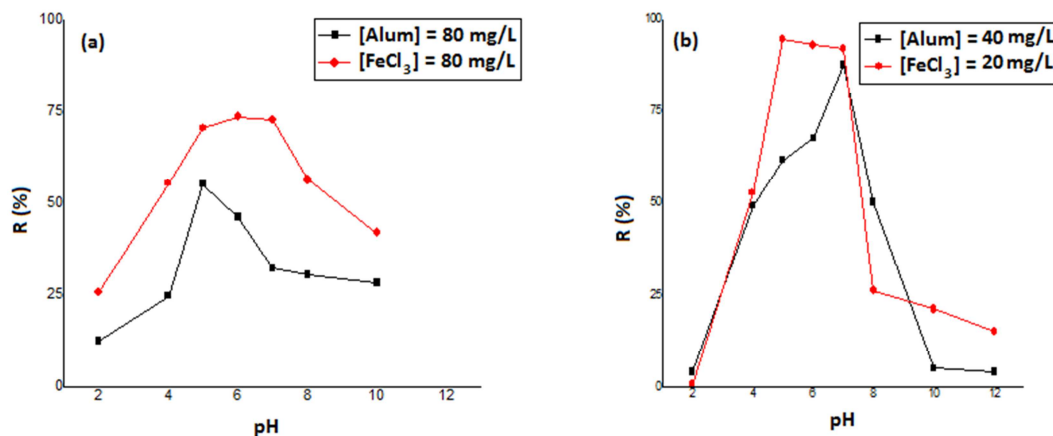

Figure 4. Effect of pH on removal of both dyes at 15 mg/L. (a) for CB and (b) for RS.
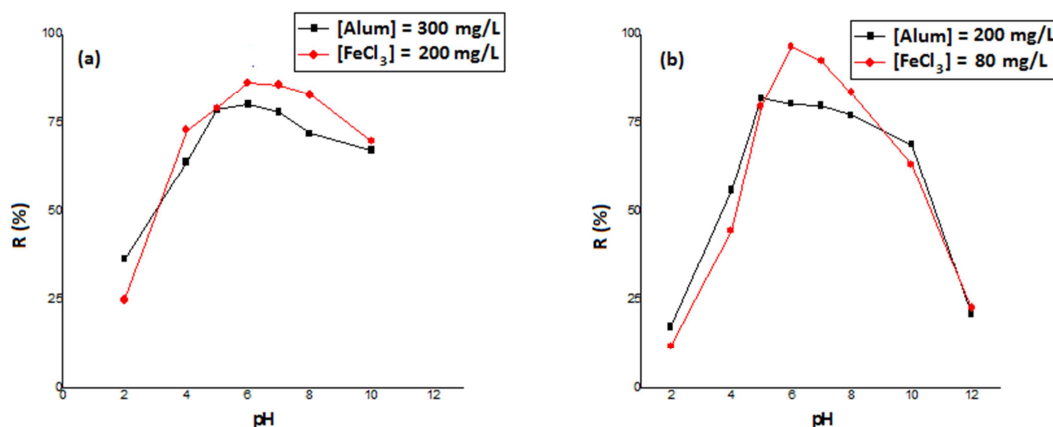

Figure 5. Effect of pH on removal of both dyes at 15 mg/L. (a) for CB and (b) for RS.

As seen in Figure 4, it appears that the removal rates of CB and RS are influenced by the pH of the solution depending on the nature of the coagulant used. We can observe that the optimum of the elimination of these compounds corresponds to an acidic pH, 6 for CB and 5 to 7 for RS.

In the case of ferric chloride, the highest removal efficiencies are recorded in the range of pH 5 to 6. Beyond this range, there is a remarkable decrease in purification efficiency.

For the CB dye, at 15 and 50 mg/L, 73 and 86% are recorded

at pH 6, respectively (Figures 4 and 5). Similarly for RS, 94 and 96% removal are obtained at pH 5 and 6, respectively. Several authors have reported higher or lower efficiencies, relative to ours, with $FeCl_3$ in similar pH ranges [6, 48].

Figures 6 (a) and (b) illustrate the different species of Fe (II) and Fe (III) present in solution as a function of pH. Since pH also conditions the chemical forms of alum and $FeCl_3$, it is clear that the mechanisms involved in the removal of organic molecules could be very diverse [4, 49]. Indeed:
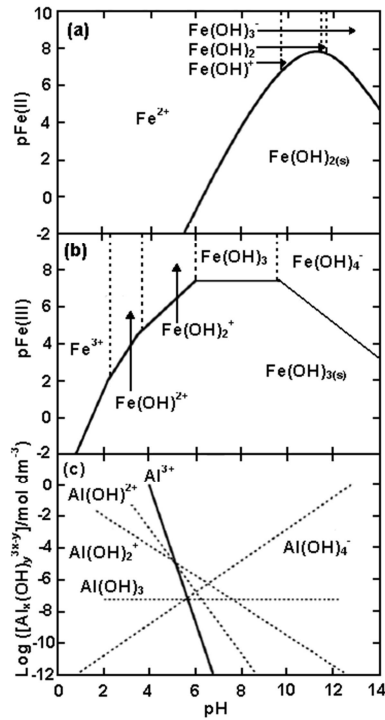

Figure 6. *Predominance-zone diagrams for (a) Fe (II) and (b) Fe (III) chemical species in aqueous solution. The straight lines represent the solubility equilibrium for insoluble Fe (OH)$_2$ and Fe (OH)$_3$, respectively, and the dotted lines represent the predominance limits between soluble chemical species. (c) Diagram of solubility of Al (III) species as a function of pH [4].*

1) At pH <6, the presence of the monomers and positively charged polymers such as Fe^{3+}, Fe $(OH)^{2+}$ and Fe $(OH)_2^+$ will cause a charge neutralization [9] of the dyes which are negatively charged resulting in direct precipitation of complexes (Fe-dye).
2) At pH between 6 and 8, where the predominant form is Fe $(OH)_{3(s)}$, a solid of amorphous structure, the dyes being negatively charged so they are trapped in the precipitates of iron hydroxides (which are positively charged).
3) At pH > 8, the predominant presence of the Fe $(OH)_4^-$ species, with the pollutant which remains also negatively charged, produces electrostatic repulsions resulting in a rapid decrease in the rate of elimination.
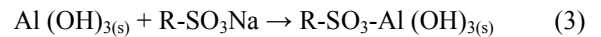
On the other hand, for alum, the highest levels of discoloration are obtained at pH values below 7.5 for the two dyes with efficiency rates of around 55 and 80% for CB at concentrations of 15 and 50 mg/L, respectively. For RS, the performances are of the order of 87 and 81% for

concentrations of 15 and 50 mg/L, respectively.

In experiments where alum is used, the aluminum ions generated by the hydrolysis can form hydroxymonomeric or polymeric complexes according to the pH of the medium. In addition, these complexes tend to polymerize between pH 4 and 7 [50]. The hydrolysis diagram of aluminum as a function of pH has also been proposed and is shown in Figure 6 (c).

At pH <5, the predominant forms of aluminum hydrolysis are: Al^{3+}, Al $(OH)^{2+}$ and Al $(OH)_2^+$. Thus, the majority presence of high valence species generates one of the possible reactions, that is, the formation of insoluble complexes between the dye and the soluble hydroxyaluminum compounds. The presence of several groups, sulfuric and carboxylic, in both structures favors this reaction which will cause a compensation of the demand of the negative charges of the dyes CB and RS. The precipitation of the insoluble Al-dye complexes will be produced [51].

At pH values between 5 and 7, the presence of the Al $(OH)_{3(s)}$ form which will adsorb the complexes formed in the aluminum hydroxide precipitates as follows:

$$Al\ (OH)_{3(s)} + R\text{-}SO_3Na \rightarrow R\text{-}SO_3\text{-}Al\ (OH)_{3(s)} \qquad (3)$$

$$(R\text{-}SO_3Na\text{–}Al\ polymeric) + Al\ (OH)_{3(s)} \rightarrow particle \qquad (4)$$

At pH > 7, the alkalization of the medium is apparently unfavorable in the case of aluminum treatment. This is mainly due to the presence of negatively charged species, such as Al $(OH)_4^-$, which decreases their attraction to anionic organic compounds.

Coagulation in acidic medium has been established to possess many advantages [52-54]. Klimiuk et al. [55] mentioned that the flocs possess a better structure and are more stable. In addition, at an alkali initial solution, the dosage of alum to attain the highest color elimination is relatively higher than at an acidic case.

3.4. Effect of Dye Concentration

In order to evaluate the role played by mass loading (or concentration) of the dye during coagulation treatment, we studied this parameter for both CB and RS dyes with both ferric chloride and alum coagulants. Thus, we can see that the increase in the initial dye content induces an increase in the percentage of elimination (see Figure 3), but also a greater demand for coagulant. The results obtained clearly show that there is a relationship between the initial concentration of the dye and the coagulant dose. This behavior can be explained by what is known as *sweep coagulation* [48, 56, 59].

It appears that the treatment of more and more colored solutions requires more complexes of metal hydroxides to coagulate the excess of the dye molecules at high concentrations. For this reason, the optimal doses are higher than those achieved with low concentrations of the dye [60, 61].

In a general manner, we observe that the elimination of SR is higher than that of CB. This is probably due to the

difference between the structures and the molecular weights of the two dyes [62, 63]. In fact, the elimination efficiencies, which are more important for RS, can be attributed to its higher molecular weight (1396 g/mol for RS and 296 g/mol for CB, Table 1) on the one hand and on the other hand to its chemical structure which contains phenolic and carboxylic functions. These functional groups could in turn affect the efficiency of the coagulation process by facilitating their removal by: (1) charge neutralization [9] and (2) floc formation, enlargement and sedimentation [37].

4. Conclusions

The main objective of this study is mainly the elimination of synthetic dyes, BF cibacete blue (CB) and red solophenyl 3BL (RS) present in the textile industry effluents by coagulation with two coagulants widely used in water industry (FeCl$_3$ and Al$_2$(SO$_4$)$_3$. 18H$_2$O). For this, we simulated the coagulation process in the laboratory using a jar test. This study allowed us to draw the following conclusions:

1. The coagulant dose is a very essential parameter for the destabilization of colloids. Indeed, the increase in the coagulant dose causes an increase in the effectiveness of physicochemical treatment to a certain optimum value. Beyond this threshold, there will be a progressive decrease in the elimination efficiency:

1) - Really, for a concentration fixed at 15 mg/L of the two dyes, the optimal doses of FeCl$_3$ are of 80 and 20 mg/L for CB and RS with elimination rates of 65 and 89%, respectively. For alum, at a concentration maintained at 15 mg/L of both dyes, a bleaching efficiency of 44 and 77% was achieved for CB and RS at optimal doses of 80 and 40 mg/L, respectively.

2) - For a concentration of 50 mg/L of both dyes, the optimal doses of FeCl$_3$ are 200 and 80 mg/L for CB and RS with removal rates of 82 and 89%, respectively. For alum, a decolorization yield of 73 and 78% was achieved for CB and RS at optimal doses of 300 and 200 mg/L, respectively.

2. Treatment with FeCl$_3$ allows more effective decolorization of the synthetic solutions containing the two dyes.

3. The coagulation process reveals various mechanisms that are complex and dependent on pH of the colored solution to be treated. For a pH comprised between 5 and 6, high elimination rates are obtained with FeCl$_3$ for the two dyes at different concentrations. The acidic pH favors a higher or lower yield at an optimal concentration of alum for the two pollutants and at different concentrations. The speciation of the coagulant depends on the pH, the concentration of the coagulant, and the mineral or organic anions in the presence. Hence, the predominant mechanisms are: charge neutralization followed by precipitation of the dye-coagulant complexes, which are insoluble, and possibly adsorption of the complexes formed in the precipitates of metal hydroxides.

4. The increase in the initial dye content induces an increase in the percentage of abatement, but also a greater demand for coagulant dose which makes it possible to demonstrate a certain stoichiometry between the coagulant dose and the initial concentration of the dye.

5. The removal of the RS dye is higher than that of the CB. This is probably due to the difference in structure and molecular weight of the two dyes.

6. As a perspective, it would be interesting to follow an application on a real effluent of the textile industry possibly containing the two dyes tested in this work.

Acknowledgements

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