Combination of coagulation-flocculation and adsorption on granular activated carbon for color removal from AR18 and real textile wastewater

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Abstract: The huge use of large amount of dyes by textile industries generates substantial pollution, especially color which is difficult to be eliminated by conventional processes. The objective of this study was to investigate the removal of Acid Red 18 (AR18) in aqueous solution and in real textile effluent through coagulation/flocculation combined with adsorption on granular activated carbon (GAC). A series of jar test experiments were carried out using different doses of the textile coagulant HYDRODEC 5D and flocculent CHTT Floc to define the optimal conditions allowing a higher removal of color. Maximum color removal reached was 23% corresponding to an ABS $_{(\lambda\ 508nm)}$ = 1.23, under the following optimal conditions of coagulation-flocculation treatment: pH=9, coagulant dose of HIDRODEC= 35 ml.L^{-1} and a flocculent dose of CHTT Floc =55 ml.L^{-1}. To improve water quality in terms of color, we applied a post treatment by adsorption on different quantities of GAC (1, 2, 3 and 4 g.L^{-1}) where a high efficiency of color elimination was obtained. To confirm our experimental results, same study was conducted on a real textile effluent. Unexpectedly, results showed that coagulation/flocculation alone was sufficient to remove (AR18) color, DCO and turbidity.

Key words: Acid Red 18, Real textile effluent, Coagulation-floculation, Adsorption, GAC.

INTRODUCTION

The textile industry is one of the most consuming of water, about 200 L of water per kg of finished textile product [1]. In Tunisia, the water consumption in this sector is 3 434 100 m^3 year^{-1} of public water and 105 000 m^3 year^{-1} of water from wells [2].This high consumption of water generates textile wastewater characterized by strong color, large amount of suspended solids, broadly fluctuating pH, high chemical oxygen demand (COD), bio toxicity and causes coloring of the receiving water environment [3].

The dyes are considered to be a major pollution problem as it is estimated that 50% of their amount are not fixed on fibers and remain finally in wastewater [4]. Azo dyes are a common industrial pollutant characterized by the presence of one or more azo group (–N=N–) [5]. A number of treatment procedures have been proposed for azo dyes degradation from wastewater using various methods: physical, such as membrane processes [6], adsorption [7], chemical such as coagulation-flocculation [8] and advanced oxidation process (AOP) [9-10], biological [11] such as aerobic and anaerobic treatment. The coagulation-flocculation and adsorption process are characterized by high efficiency in removal of color of waste water containing dyes with azo chromophore. Coagulation-flocculation was conducted for the treatment of industrial wastewater to achieve maximum removal of COD and TSS. Therefore, investigated the effect of coagulation dose, pH of solution and polyelectrolyte as coagulant aid for effective treatment of industrial wastewater [12-13]. Aluminum sulfate (alum), ferric chloride, ferrous sulfate was commonly used as coagulants

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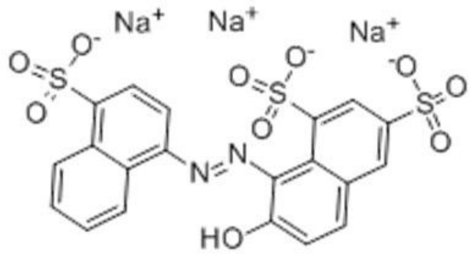

Figure 1: Chemical structure of AR 18.

Table I : Physico-chemical characteristics of AR18.

Parameter	value
Color index	AR18
Chemical formula	$C_{20}H_{11}N_2Na_3O_{10}S_3$
Molecular Weight (g.mol^{-1})	604.47
λ max (nm)	508
Absorbance (λ_{508})	1.61

[14]. Adsorption is an efficient and economically feasible process for treatment of wastewater containing chemically stable pollutants [15-16]. Activated carbon is widely used for adsorption of organic compounds and hardly biodegradable substances [14]. However, these processes are only considered not very effective for effluent treatment in some cases. One alternative would be the application of these techniques in combination with conventional treatments. The objective of this study was to evaluate the efficiency of a coagulation-flocculation combined with adsorption as post-treatment for the removal of AR 18 from a synthetic and real textile effluent.

MATERIALS AND METHODS

1. Materials

Textile dye used is a commercial azo dye Acid Red 18 (AR18) used in solution form. Distilled water was used to prepare a solution of 50 mg.L^{-1} AR18. Figure 1 gives the chemical structure of AR18.
The main characteristics of the dye are presented in table I.
Real textile effluent was issued from wash and tannery water collection basin of a Tunisian textile industry.
HIDRODEC 5D and CHTT floc were in commercial grade. Coagulant was purchased in liquid form when flocculant was in solid form. HIDRODEC 5D was cationic polyamine, pH=5± 1 at 20°C. CHTT Floc was soluble in water with pH=8± 1. Both of coagulant and flocculant were used in the experiments in solution form prepared with distilled water.
Granular activated carbon was in analytical grade and supplied by LOBA company. It has a granular about 1.5 mm.

2. Instruments

Jar test used was Fisher scientific apparatus that consisted of four paddles. A pH-meter Consort C561 was used to control pH of the solutions. Turbidity was measured by turbidity meter PCE-TUM 20 with a range of 0-1000 NTU (nephelometric turbidity unit).
COD is determined by digestion in a thermoreactor of type WTW CR 2200, and then measured using a photometer on the wavelength λ 420 nm for the range 0-150 mg/L and on the Wavelength λ 620 nm for the range 0-1500 mg.L^{-1}.
The UV-visible spectra were determined on a spectrophotometer (PerkinElmer LAMBDA 35) after and before treatment wavelength between 400 and 800 nm.

3. Cogulation-flocculation Jar-test procedure

All coagulation flocculation experiments were performed in jar test at room temperature (average 25±2^{oC}). A series of jar test experiments were carried out using different doses of coagulant and flocculant to define the optimal conditions of pH and dose of coagulant. Beakers were filled with 500 ml of synthetic effluent; pH was adjusted at the desired values between 8 and 11 using NaOH 1M or HCl 1M. A coagulant dose added varies between 35 and 105ml coagulant.L^{-1} at rapid mixing (120 rpm) during 5 min. Then we reduced the mixing speed to 30 rpm during 30min and while adding dose of flocculant.
The solution was decent (2hour) then filtered and the concentration of the filtrate was determined by spectrophotometer analysis.

4. Adsorption experiments

The experimental adsorption tests were carried out in batches with the synthetic effluent (effluent treated after the coagulation/ flocculation process) using GAC as the adsorbent, The adsorption experiments were conducted by adding different concentrations (1 g.L^{-1}, 2 g.L^{-1}, 3 g.L^{1} and 4 g.L^{-1}) of GAC, into Erlenmeyer flasks containing 300 ml of synthetic effluent after a optimal coagulation treatment conditions and pH adjustment. All effluents are stirred at the same stirring speed with the multiple stirrer VELP SCIENTIFICA at constant temperature (25°C). Samples are taken in intervals time varies between 15 and 120 min then filtered under vacuum using a membrane with 0.45 µm of porosity. The filtrate's absorbance was determined by means of the UV spectrophotometer adjusted at λ_{max} (508 nm) of the AR18 dye.

4.1. Adsorption Isotherm

Adsorption isotherms describe the relationship between the equilibrium amount of solute adsorbed on adsorbent and the amount of remaining solute. The Freundlich and langmuir models were employed to analyze the relation between the amount of dye adsorbed and its equilibrium concentration.

4.1.1. Freundlich Isotherm

The Freundlich isotherm [17] is an empirical equation employed to describe the multilayer adsorption. This model predicts that dye concentration on the adsorbent will increase with the increase of the adsorbate concentration in the solution.

Freundlich equation (1) is expressed as the following:

$$q_e = K\, C_e^{1/n} \qquad (1)$$

Where

q_e: The amount adsorbed at equilibrium (mg.g^{-1}).

K and n are Freundlich constants (L.g^{-1}).

C_e: the equilibrium concentration of the adsorbate (mg.L^{-1}).

A linear form of the Freundlich equation is generally expressed as follows (Equation 2):

$$\mathrm{Ln}\,(q_e) = \ln K + 1/n\ \mathrm{Log}\ C_e \qquad (2)$$

4.1.2. Langmuir Isotherm

Langmuir isotherm [18] theory assumes that the monolayer coverage of adsorbate is over a homogeneous adsorbent surface where all sorption sites are found to be identical and energetically equivalent. Langmuir equation (3) is expressed as the following:

$$\frac{Q}{Q_{max}} = \frac{K\,C_e}{1+K\,C_e} \qquad (3)$$

The linearization of the Langmuir equation can be presented as an equation (4).

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}\,K\,C_e} \qquad (4)$$

Where:

Q: The adsorbed amount by material (mg.g^{-1}).

C_e: Solution concentration at equilibrium (mg.L^{-1}).

Q_{max}: Maximum adsorbate quantity of adsorbed on the surface of the adsorbent at equilibrium (mg.g^{-1}).

K: Langmuir Constant or the equilibrium adsorption constant.

4.2. Kinetic Models

4.2.1. Pseudo-first order kinetic

Pseudo-first order kinetic [19] is described by the following equation (5)

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{K_1}{2.303}\, t \qquad (5)$$

Where:

q_e: Adsorbate amounts at equilibrium (mg.g^{-1}).

q_t: Adsorbate amounts at time t (mg.g^{-1}).

k_1: constant rate (min^{-1}).

4.2.2. Pseudo-second order kinetic

Pseudo-second order kinetic [20] is expressed as the following equation (6):

$$\frac{dq_t}{dt} = k_2\,(q_e - q_t)^2 \qquad (6)$$

Where:

q_e: the amounts of adsorbate at equilibrium (mg.g^{-1}).

q_t: the amounts of adsorbate at time t (min) (mg.g^{-1}).

k_2: the constant rate (g.mg^{-1}.min^{-1}).

Integration of the Equation (9) at the boundary of qt=0 at t=0 and qt=qt at t=t, the equation can be converted to the linear form as follows:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (7)$$

The percentage removal of color and COD was respectively determined using the following equation (8) and (9):

$$\%\ \text{Color removal} = \frac{ABSi - ABSf}{ABS\ i} * 100 \qquad (8)$$

Where:

ABS_i: The initial absorbance of dye (mg.L^{-1}).

ABS_f: The final absorbance of dye (mg.L^{-1}).

$$\%\ \text{COD removal} = \frac{CODi - CODf}{COD\ i} * 100 \qquad (9)$$

Where:

COD_i: The initial COD of dye (mg.L^{-1}).

COD_f: The final COD of dye (mg.L^{-1}).

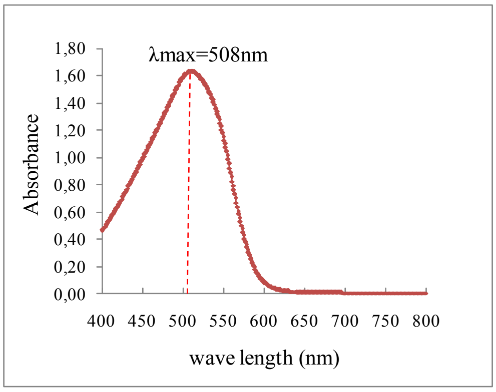

Figure 2: Absorbance curve of Acid Red 18 (50 mg.L^{-1})

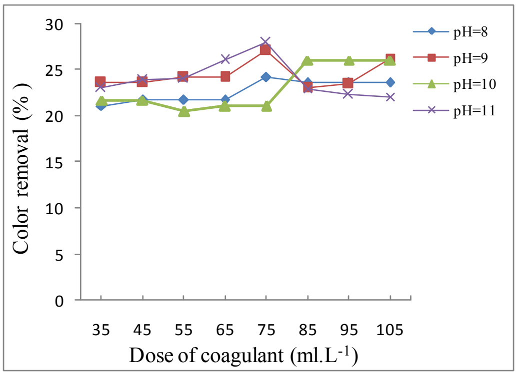

Figure 4: Effect of coagulant dose and pH on the variation of color removal

RESULTS AND DISCUSSION

The wavelength corresponding to the maximum absorbance (λ max) and the calibration curves at λ max of the dye were determined. The absorbance curve was carried out for 50 mg.L^{-1} solution and the calibration curve was carried out at concentration ranging from 5 to 80 mg.L^{-1}.

Figure 2 shows the absorbance curve of 50 mg.L^{-1} of AR18 dye at a wave length range from 400 to 800 nm, where λ max is 508 nm.

Figure 3 shows the calibration curve of AR18 dye in linear relationship.

1. Treatment by coagulation-flocculation

The determination of the optimum dose of coagulant and pH is an essential parameter for the destabilization of the colloids and the removal of color [21]. Figure 4 shows the effect of coagulant dose and pH on the variation of color removal. The best performance in term of color removal was at pH=9 and pH=11, where color removals were respectively 27% and 28% using 75ml.L^{-1} of coagulant. The increase of the coagulant didn't favor the stabilization of the colloids or the elimination of color. Table II shows the percentage of the elimination of color at different pH and different doses of added coagulant.

At the optimum pH equal to 9, the rate of color elimination increases progressively in function of the dose of coagulant added which varies from 23% with the dose 35 ml.L^{-1} and 27% with the dose 75ml.L$^{-1,}$ However the difference of values of color elimination didn't exceed 4% between the minimum and the maximum of added doses of coagulant, so what we chosen the lower amount as an optimal dose of treatment.

2. Adsorption on GAC

2.1. Color removal

The Coagulation-flocculation process eliminates only 23% of the color of the synthetic effluent AR18. We applied a post-treatment by adsorption

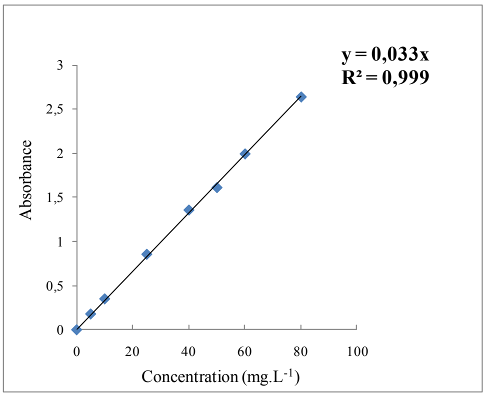

Figure 3: Calibration curve of Acid Red 18 concentration at λ max=508nm

Table II: Effect of coagulant dose and pH on removal of AR18 dye

Color removal (%) of Acid Red 18								
pH	**Coagulant dose (ml.L^{-1})**							
	35	45	55	65	75	85	95	105
8	21.1	21.7	21.7	21.7	24.2	23.6	23.6	23.6
9	**23.6**	23.6	24.2	24.2	**27.1**	23.0	23.5	26.3
10	21.7	21.7	20.5	21.1	21.1	26.1	26.1	26.1
11	23.0	23.9	24.1	26.0	28.0	23.0	22.4	22.1

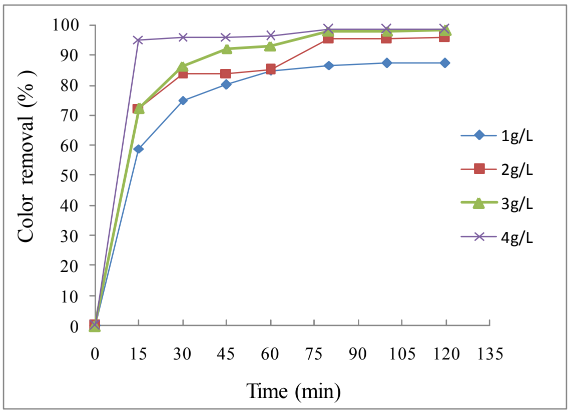

Figure 5: Variation of color removal in function of time

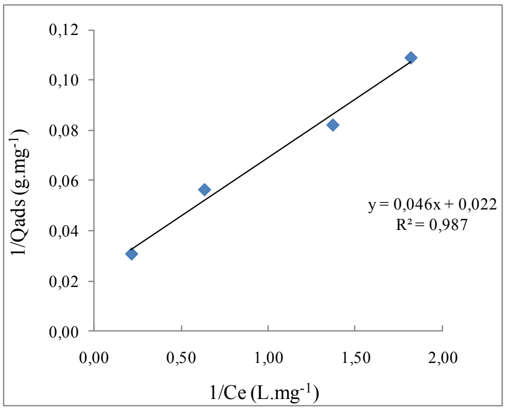

Figure 7: Langmuir isotherm model

on GAC to improve the rate of discoloration. The adsorption tests were carried out on samples of water treated by coagulation flocculation under the optimum conditions: pH = 9 and coagulant dose = 35ml.L^{-1}.

Figure 5 shows the variation of color removal in function of time. After 15 min of contact of dye AR18 with the different masses of GAC, color removal was respectively 58% for 1g.L^{-1}, 72% for 2 and 3g.$L^{-1}$and 95% for 4g.L^{-1}. The removal of color increased by an increase in contact time up to 120 min was respectively 87% for 1g.L^{-1}, 95% for 2g.L^{-1} and 98% for 3 and 4g.L^{-1}.

2.2. kinetics and isotherms model

The results obtained by the adsorption of AR18 dye were analyzed by the models of Langmuir and Freundlich (Figure 6, 7).

Parameters of Freundlich and Langmuir isotherms are sited in table III. The results showed that AR18 dye on GAC fitted according to Freundlich isotherm model (R^2 =0.991).

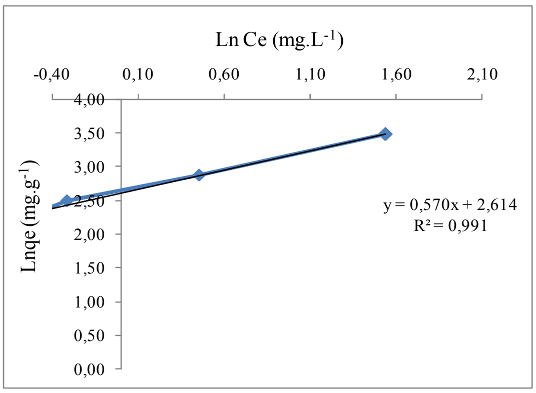

Figure 6: Freundlich isotherm model

The conformity of experimental data with the pseudo-first order and pseudo-second order models can be determined by the correlation coefficient (R^2) table IV. The pseudo-First order kinetic models best describe the adsorption of AR18 onto CAG.

Figure 8 present the degradation of color of AR18 after the treatment by C/F and after the adsorption on 1 g of GAC about 2 hours.

3. Treatment of real textile waste water

3.1 Color removal

Real textile waste water used to evaluate the efficiency of sequencing coagulation-flocculation and adsorption processes based on the optimum operational parameters obtained during the removal of AR18. The characteristics of real textile wastewater are presented in table VI.

Table III: Parameters of Freundlich and Langmuir isotherms

	Langmuir Parameters			Freundlich Parameters		
	k_L	Q	R^2	K_f	N	R^2
AR18	0.478	45.45	0.987	3.71	0.570	0.991

Table IV: Adsorption kinetic model constants of AR18

Dye	Pseudo First-order model		Pseudo Second-order model	
	R^2	K_1	R^2	K_1
AR18	0.991	-0.023	0.790	0.047

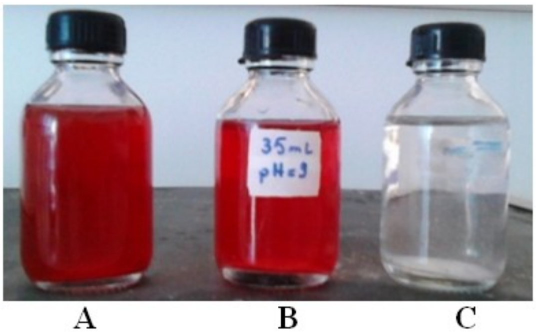

Figure 8: ACID RED 18. A: Raw Effluent, B: After C/F, C: After adsorption on 1 g of GAC (2h)

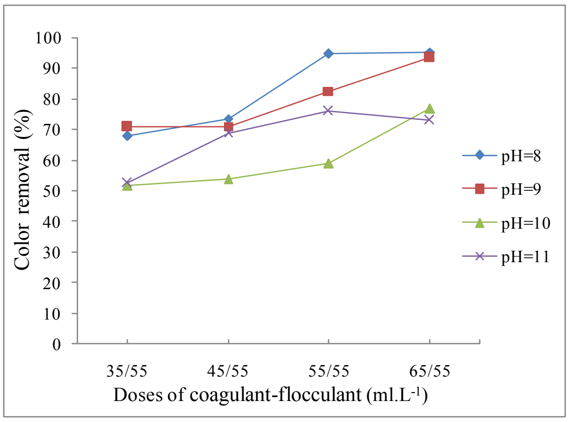

Figure 9: Effect of coagulant dose and pH on color removal

Jar-test results using the dose of coagulants varies between 35 et 65ml.L-1 and the dose of flocculant 55ml.L^{-1} at adjusted pH values varied between 8 and 11, indicated the color removal rate is improved with the addition of doses of coagulant figure 9 present the effect of the doses of coagulant and pH on the elimination of color.

The coagulation/flocculation efficiency and the quality characteristics of treated effluents depended on the amount of coagulant and pH. The maximum color removal at the pH equal to 8 (the initial pH of the effluent) and pH equal to 9.

At pH=8 the rate of color removal is 68% and 73%, corresponding respectively to the doses 35.45 ml.L^{-1} and 95% for the doses 55 and 65ml.L^{-1}. At pH=9 the rate of color removal is 70%, 71%, 82% and 93% corresponding respectively to the doses 35, 45, 55 and 65ml.L^{-1}.

3.2. Turbidity removal

The water is considered clear if the turbidity is less than 5NTU [22]. Figure 10 presents the variety of the turbidity in function of coagulant dose and pH. The turbidity of reel textile effluent decreases in function of the dose of added coagulant. The lower turbidity value was recorded at pH = 8 with the dose of coagulant 55 and 65 ml.L^{-1} which is less than 5 NTU.

3.3. COD removal

Chemical oxygen demand shows the organic pollution existing in the textile effluent. For this we follow the degradation of the COD in function of the dose of added coagulant and the pH. Figure 11 presents the variety of removal of COD in function of doses of coagulant-flocculant and pH. COD degradation rates increase slightly with the added coagulant dose. The lower rate of COD elimination recorded was obtained when using 35 ml dose of coagulant, for different pH values (8, 9, 10 or 11). Using other doses (45, 55 and 65 mL.L^{-1}), COD removal was about 60% for all the pH used.

Table VI: Characteristics of real textile effluent and the Tunisian norms of the effluent rejects in public canalizations (ONAS)

Parameters	Real textile effluent	Norms NT106.02
T (° C)	35	25-35
PH	8.0	6.5-9
Absorbance (λ_{508nm})	0.36	-
Turbidity (NTU)	127	-
COD (mg.L^{-1})	1273	1000

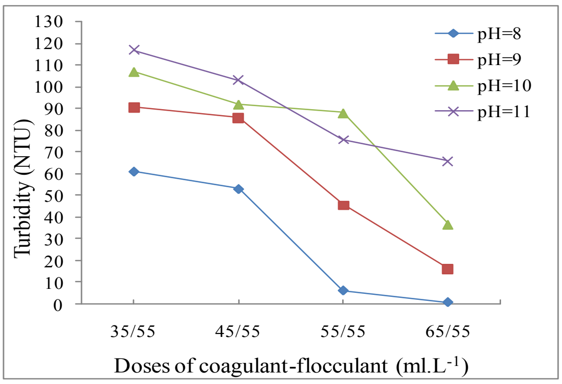

Figure 10: Variation of turbidity in function of coagulant-flocculant dose and pH

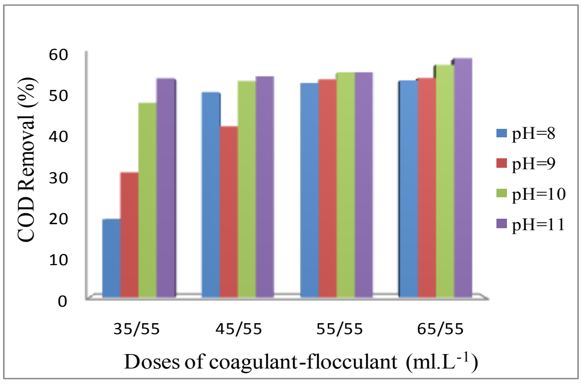

Figure 11: Variation of COD removal in function of coagulant-flocculant dose and pH

3.4. Effect of initial pH

The pH of the effluent varies very slightly in function of the dose of added coagulant. Figure 12 shows the variation of pH after the treatment by coagulation-flocculation. High pH values before treatment (pH = 10 and pH = 11) did not favor the elimination of color, turbidity and COD.

For the real textile effluent the optimum conditions of treatment was obtained when the pH equal to 8 and the doses of coagulant and flocculant were both equals to 55ml.L^{-1}. In these conditions, color removal rate was equal to 95%, turbidity equal to 6.5 NTU and COD equal to 601mg.L^{-1}.

CONCLUSION

This study shows that a combination of coagulation with adsorption on GAC for the discoloration of AR18 textile dye was more efficient than C/F alone. AR18 textile dye is partially eliminated by a C/F process in term of color. The optimal conditions of C/F treatment found at pH=9, the coagulant dose of HIDRODEC

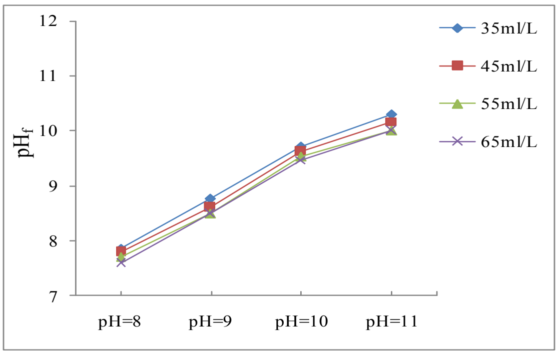

Figure 12: Variation of pH after treatment by coagulation-flocculation

5D equal to 35 ml.L^{-1} and a flocculant dose of CHTT Floc equal to 55 ml.L^{-1} which the color removal efficiency was 23%. When adding granular activated carbon adsorption as post treatment, a high efficiency of color are obtained (87% for 1g.L^{-1}, 95% for 2g.L^{-1} and 98% for 3 and 4g.L^{-1}). A freundlich adsorption isotherm model was used for the description of the adsorption equilibrium and the first-order kinetic equation could best describe the adsorption kinetics of AR18 dye onto GAC.

The degradation of acid red dye 18 in a real textile effluent requires only simple treatment by C/F without need of post treatment to reach a total discoloration.

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NOMENCLATURE

C/F: Coagulation-flocculation
GAC: Granular activated carbon
AR18: Acid Red 18
COD: chemical oxygen demand
rpm: round per minute
λ max: Maximum wavelength
NTU: Nephelometric turbidity unit

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