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Diagnosis and characteristics of water quality along the Wadi El Bey river (Tunisia). Coagulation/flocculation essays of textile effluents discharged into the Wadi

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ABSTRACT

In the present investigation, Wadi El Bey river (Tunisia) was studied for water quality. Various physicochemical parameters (temperature, pH, conductivity, TSS, DO, COD, BOD_5, ammonia, nitrate, phosphate, color, Pb, Zn, Ni, Cu, Cr, Fe, and Al) and microbiological (*Fecal coliforms*, *Fecal streptococci*, *Escherichia coli* (*E. coli*), *Salmonella*, *Staphylococcus*, and *Pseudomonas*) analysis of freshwater body were performed during 3 years (2012–2015) and compared to Tunisian standard (TN-106-02). Thirteen sampling sites were chosen to study the effect of industrial and domestic effluents on the river. Results revealed that almost all of the parameters exceed TN-106-02 standards indicating that the water quality of the river presents a high risk and it is urgent to control and to treat the wastewater discharged into Wadi El Bey. In this paper, several coagulation/flocculation essays are studied and evaluated on industrial wastewater effluents (site S1) discharged into the river. Using response surface methodology to evaluate the interactions between three factors (concentration of coagulant, flocculant dosage, and initial pH) on the treatment, the optimal conditions were reached by removing 87.87% of COD and decolorization of the water to 99.82%. This optimal treatment was obtained with 275 and 75 mg L^{-1} doses, respectively, for coagulant and flocculant.

Keywords: Coagulation–flocculation; Tunisia; Decolorization; Industrial wastewater; Response surface methodology (RSM); Wadi

1. Introduction

Rivers are the most important natural resources for human development. Unfortunately, river waters are being polluted by indiscriminate disposal of sewage, industrial waste, and plethora of human activities, which affects their physicochemical and microbiological quality [1,2]. The potential cause of degradation of river water quality is due to various point and non-point sources [3,4]. Due to the increasing problem of deterioration of river water quality, it

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is necessary to monitor water quality to evaluate the production capacity [5]. The watershed of Wadi El Bey (475 km^2) is located in the northeast part of Tunisia and drains Grombalia, Beni Khaled, and Soliman plains. This region is characterized by a semi-arid to sub-humid Mediterranean climate, with an annual precipitation average value of 500 mm [6]. The two major effluents of Wadi El Bey river are Wadi Maleh and Wadi Tahouna. The main sources of pollution of Wadi El Bey river are industrial effluents (textile, tannery, food industries, etc.), agricultural drainage, urban, and touristic wastewater after or without treatment, domestic sewage along with excreta by human being and various warm-blooded animals which are directly or indirectly discharged into the river and natural sources. These sources of pollution have adversely affected the physicochemical and microbiological quality of the river (Fig. 1).

Physicochemical parameters such as temperature, pH, dissolved oxygen (DO), salinity, organic matter (e.g. COD, BOD_5), and nutrients (nitrogen "N" and phosphorus "P") have been reported to influence biochemical reactions within water systems [7]. Such changes in the concentration of these parameters are indicative of changes in the condition of the water system [8]; the consequence of such is the compromise of the water quality for beneficial uses. Microbiological pollution can be caused by point sources like discharges of treated or untreated sewage from human sources or livestock enterprises and by non-point sources like urban and agricultural runoff or waterfowl. The presence of microbial pathogens (*Escherichia coli* (*E. coli*) and total *coliform*) in polluted, untreated, and treated waters poses a considerable health risk to the public. *Coliform* bacteria are used as microbiological indicators for water quality. Freedom from contamina-

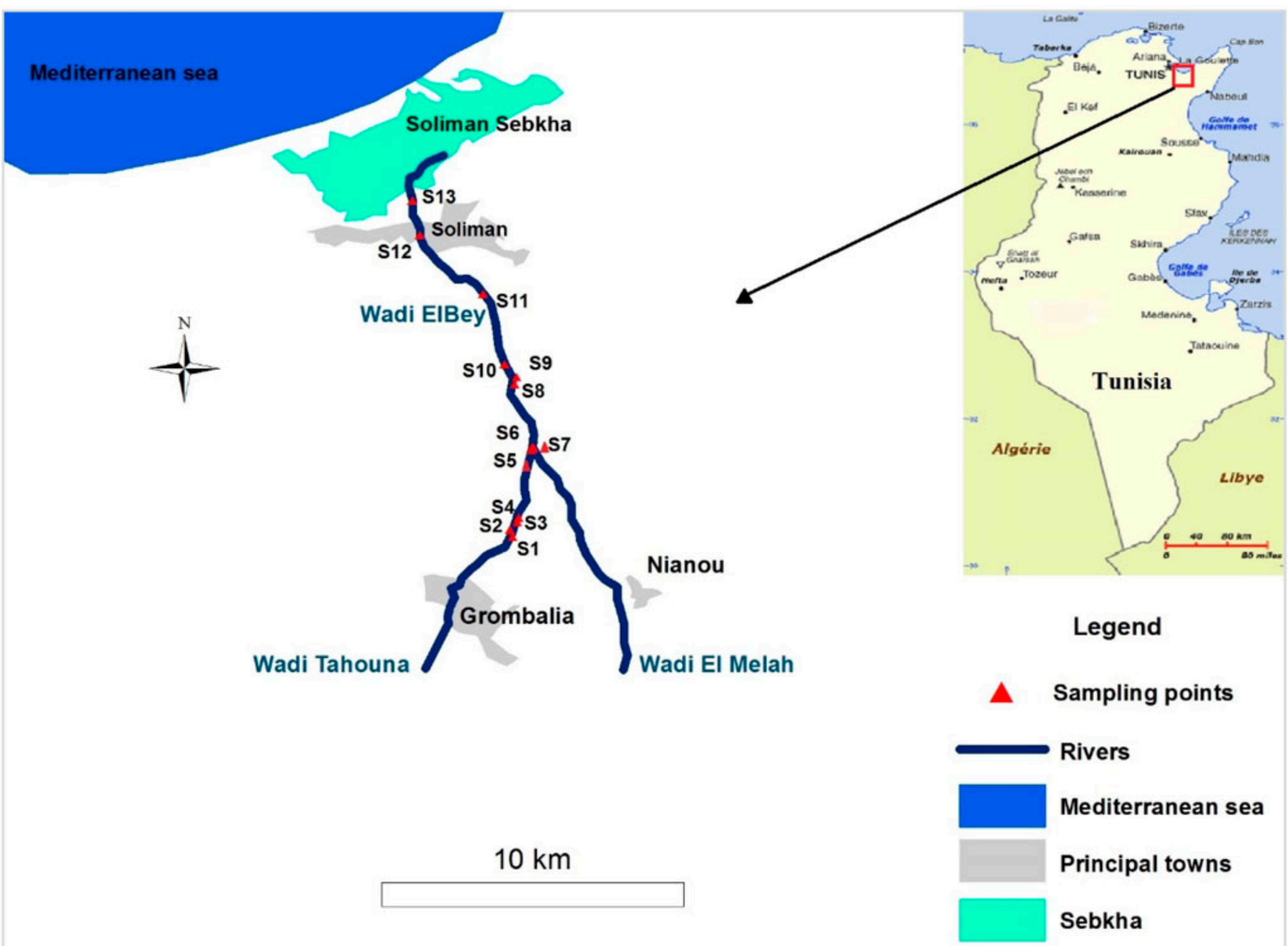

Fig. 1. Map of the watershed of Wadi El Bey river and sampling locations (Global Positioning System type Garmin).

tion with fecal matter is the most important parameter of water quality because human fecal matter is generally considered a greater risk to human health, as it is more likely to contain human enteric pathogens [9]. The presence of toxic metals (such as Pb and Cu) in the environment has been a source of fret to environmentalist, government agencies, and health practitioners as a result of their health implication that is hazardous and toxic to man [10]. The presence of these metals in the aquatic ecosystem has far-reaching consequences on the biota and man; their toxic effects on man are related to dermal, lung, and nasal sinus cancers [11]. Prevention of river pollution requires effective monitoring of physicochemical and microbiological parameters [12,13]. Few investigators have worked on heavy metal pollution of Wadi El Bey river [14]. However, there is no report pertaining to exploration the physicochemical and microbiological pollution in the Wadi El Bey river, hence the need for this study.

The primary aim of this study was to evaluate the physicochemical pollution, the presence of heavy metals, and the microbiological quality of the water in Wadi El Bey river over three years period (2012–2105). These findings will reveal the effects of the rural population and industries situated along the river on its water quality.

The secondary aim of the present investigation was to determine the maximum depollution ability of the coagulation/flocculation (CF) treatment of Grombalia industrial effluents directly discharged into Wadi El Bey river adopting a full range of response surface methodology (RSM) using central composite design (CCD) model to analyze the efficiency of the system under different conditions.

2. Materials and methods

2.1. Study area and sampling

The catchment of Wadi El Bey (475 km^2) is located in the northeast of Tunisia. The Wadi drains Grombalia, Beni Khaled, and Soliman plains. This Wadi is the largest permanent stream flowing in the region. It runs through a large agricultural area and receives urban (domestic and industrial) discharges erected throughout the Wadi that will be eventually evacuated in Soliman Sebkha and subsequently in the sea [15,16].

Thirteen monitoring sites (Fig. 1, Table 1), which cover a wide range of the entire watershed of Wadi El Bey river, constituted the water quality-monitoring network, and were thus used to represent the water quality of the region. The sampling areas were chosen according to the anthropogenic activities and the eventual sources of the river contamination. The sites were monitored twice per season during 3 years (2012–2015). During the study period, 24 sets of samples were taken for each site (Fig. 1). The sampling points were chosen in order to identify the impact of each source of pollution on the physicochemical and microbiological quality of the Wadi El Bey by sampling in the four seasons and under the full range of temperature values. Prior to sampling, bottles were autoclaved, washed with double-distilled water and before actual sampling these bottles were rinsed with wastewater to be sampled. Sampling, preservation, and transportation of the water samples to the laboratory were according to standard methods (APHA) [17]. All samples were stored at 4°C and analyzed within 48 h of sample collection.

Table 1
Identification of sampling sites along Wadi El Bey river

Sites	Identification of sampling sites	Latitude	Longitude
S1	Discharge of Grombalia industrial area	36°36´37.18´´N	10°29´57.70´´E
S2	Discharge of beer industry (SONOBRA)—Grombalia	36°36´38.52´´N	10°29´59.15´´E
S3	Treated wastewater—WWTP Grombalia	36°36´39.00´´N	10°30´00.42´´E
S4	Discharge of Grombalia Tannery	36°36´40.81´´N	10°30´2.16´´E
S5	Bridge over Wadi El Bey	36°38´24.18´´N	10°30´59.70´´E
S6	Agricultural drainage—Wadi Maleh	36°38´29.96´´N	10°31´6.97´´E
S7	Bridge over Wadi Maleh before Wadi El Bey	36°38´29.55´´N	10°31´5.14´´E
S8	Wadi El Bey Before WWTP discharges—Béni Khaled	36°39´32.52´´N	10°30´37.49´´E
S9	Agricultural drainage—Béni Khaled	36°39´34.56´´N	10°30´36.75´´E
S10	WWTP discharges—Béni Khaled	36°39´35.18´´N	10°30´35.75´´E
S11	Bridge over Wadi El Bey, road Soliman——Grombalia	36°41´3.39´´N	10°29´34.96´´E
S12	Bridge over Wadi El Bey, Soliman city	36°41´42.51´´N	10°28´47.19´´E
S13	Wadi El Bey Before Sebkha	36°43´22.03´´N	10°28´21.94´´E

2.2. Physical chemical analysis

For all samples collected, parameters such as pH, electrical conductivity (EC), temperature (T°), and DO values were *in situ* measured using pH meter type WTW pH170i; conduct meter type WTW Condi 170i and oxymeter type WTW oxi 170i, respectively. The water samples were analyzed in laboratory for nitrate (NO_3^-), ammonium (NH_4^+), total phosphorus (TP), total nitrogen (TN) chemical oxygen demand (COD), 5-d biochemical oxygen demand (BOD_5), and total suspended solids (TSS) following the standard methods [17]. Concentration of heavy metals (iron (Fe), aluminum (Al), nickel (Ni), lead (Pb), chromium (Cr), zinc (Zn), and copper (Cu)) in water samples were carried out using the optical emission spectrophotometry according to the Standard method NT ISO 11885 (2007). Average values of three replicates were taken for each determination.

2.3. Biological analysis

For microbiological analysis, the samples were collected in sterilized glass-stoppered bottles and transported to the laboratory under refrigerated conditions. The density of the *Fecal coliforms* (FC), *Fecal streptococcus* (FS), and *E. coli* were determined by multiple tube fermentation technique following standard methods [17]. *Salmonella Shigella* (SS), *Pseudomonas aeruginosa,* and *Staphylococci* were isolated using specific media according to standards methods [17]. The number of all isolated bacteria was expressed as colony-forming units (CFU) per 100 mL of analyzed water.

2.4. Coagulation/flocculation experiments

The coagulation/flocculation (CF) experiments were conducted by a series of standard four-beaker jar test apparatus (Bio block, Scientific, floculateur 10405) equipped with four one-liter beakers. Each beaker contained 300 mL of Grombalia industrial wastewater (S1). Six chemical coagulants: lime slurry ($CaCO_3$), aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and ferrous sulfate ($FeSO_4$), and two flocculants: polyacrylamide and CHT-flocculant CV were tested on their COD removal and decolorization capability. Each coagulant was added separately and rapidly mixed at 180 rpm during 3 min. Then, flocculant was added and the speed was reduced to 30 rpm for 15 min. Afterwards, particles were settled down for about 15 min [18]. After settling, samples were taken for analysis. HCl and NaOH were used for pH adjustment.

2.5. Optimization of CF process using RSM approach

To optimize the CF treatment of industrial wastewater discharged in the Wadi, a CCD model based on three factors was used as experimental design model (Table 2). Coagulant concentration (125–275 mg L^{-1}), flocculant dosage (25–75 mg L^{-1}), and pH (5–9) were taken as input variables. The experiments were performed in random order to avoid systematic error. Three-level Box–Behnken full factorial design was employed to optimize the CF treatment of the industrial wastewater [18]. Coagulant ($X1$), flocculant ($X2$), and pH ($X3$) were taken as input variables (Table 2).

A total of 29 experiments were performed. Experimental data obtained from the CCD model experiments can be stated in the form of the following Eq. (1):

$$Y = \alpha_0 \sum \sum_{i=1}^{k} \alpha_i X_i + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \alpha_{ij} X_i X_j + \sum_{i=1}^{k} \alpha_{ij} X_i^2 + \varepsilon \quad (1)$$

where α_0 is the constant, α_i is the linear effect of the input factor X_i, α_{ij} is the linear by linear interaction effect between the input factors X_i, X_j, α_{ij} is the quadratic effect of input factor X_i, and ε is the error [19].

The statistical analysis of CCD experimental results, response surface modeling, and optimization of process variables were carried out using statistical NemrodW software (version 2000-D).

Table 2
Experimental range and levels of independent factors

Coded factors	Factors	Coded levels		
		+1	0	−1
$X1$	Coagulant concentration (g L^{-1})	275	200	125
$X2$	Flocculant dosage (g L^{-1})	75	50	25
$X3$	pH	9	7	5

2.6. Phytotoxicity study

Phytotoxicity was assessed by determination of the germination index (GI) of lettuce (*Lactuca sativa*) according to Zucconi et al. [20] standard method. Twenty seeds were uniformly placed in a Petri dish which contained a Whatman paper filter. Five milliliters of sample of untreated and of treated industrial wastewater using CF process was poured into Petri dish and incubated for seven days at 25˚C. Distilled water was used for control tests. The GI was calculated based on the Eq. (2) [21]:

$$GI = \%G \times \frac{LS}{LC} \quad (2)$$

where %G is the number of germinated seeds expressed as percent of control values, LS is the average value of root length in sample, and LC is the average value of root length in the control. All experiments were carried out in duplicate.

3. Results and discussion

3.1. Wastewater characterization

Water quality can be impacted through its many facets (physical, including temperature and turbidity; chemical, including pH and concentrations; biological, including biodiversity and species abundance, across the entire food web from microbial pools and macrophytes up to fish). In the present study, various physicochemical, microbiological, and heavy metals analyses were studied to evaluate variations in water quality. Tables 3–4 summarize the water quality along the Wadi El Bey river.

3.1.1. Monitoring of physicochemical parameters

3.1.1.1. Temperature. Temperature may affect the chemical and biochemical reactions and the solubility of gasses in the water. Consequently, strong unpleasant odor from water may reflect the release of dissolved gasses at high temperatures [22]. Cooler water in a stream is generally considered healthier than warmer water, but there are no definitive standards. According to Table 3, the average water temperature recorded was ranged from 12.2˚C (site S9) to 26.2˚C (site S1). The results showed relatively slight local variations in surface temperature excluding the areas exposed to a thermal pollution, as site S1, which recorded the maximum annual temperature of 29.5˚C in summer that exceeds the maximum permissible value of 25˚C required by the Tunisian standards (TN-106-02) [23]. This may be due to the water discharge of the Grombalia industrial area that is mainly textile wastewater characterized by high temperature.

3.1.1.2. pH. pH is a measurement of the acidity or basic quality of water. At extremely high or low pH levels (for example 9.6 or 4.5), the water becomes unsuitable for most organisms. Most aquatic organisms adapt to a specific pH level and may die if the pH of the water changes even slightly.

The pH of surface water is important to aquatic life because pH affects the ability of fish and other aquatic organisms to regulate basic life-sustaining processes, primarily the exchanges of respiratory gasses and salts with the water in which they live. On the other hand, bacteria's activities and decomposition of organic matters can contribute to raise the pH. In addition, the discharge of domestic and industrial wastewater can affect the pH of the receiving environment [24,25]. In the study area, no significant pH difference was recorded between sites. Otherwise, pH mean values of water samples range between 6.9 for discharge of Grombalia Tannery site (S4) and 8.3 for discharge of Grombalia industrial area (S1) indicating that Wadi El Bey Water was neutral to slightly alkaline in nature. These values were within maximum permissible limit of 6.5–8.5 prescribed by WHO [26] and required by Tunisian standards (TN-106-02). Based on these guidelines, the pH of the river water would not adversely affect its use for domestic or recreational purposes. A comparison with an earlier report by Khadhar et al. [14] on the same study site showed some similarities with maximum pH of 8.33 obtained at an industrial Site (R1) and 8.01 obtained at a WWTP discharge (R2) in their study.

3.1.1.3. Dissolved oxygen. DO in water is essential for aquatic life. Deficiency of DO gives bad odor to water due to anaerobic decomposition of organic waste [27]. In the case of DO, standard for sustaining aquatic life is 4 mg L^{-1}, whereas for drinking purposes it is 6 mg L^{-1} [28]. In the present investigation, DO average values were fluctuated between 1.5 mg L^{-1} (S4) and 4.9 mg L^{-1} (S6). The lowest concentration of DO was measured for the discharge of Grombalia Tannery site (S4), while the highest value was detected in the Bridge over Wadi Maleh before Wadi El Bey site (S6). The low values of DO were an indicator of the presence of high organic loads generated by industrial wastewater [29] and the degradation of the organic matter by micro-organisms [2,30].

3.1.1.4. Electrical conductivity. EC in water is affected by the presence of inorganic dissolved solids such as

Table 3
Summary of physicochemical analyses on water samples of Wadi El Bey river

Site		T (°C)	pH	CE (mS/cm)	DO (mg L^{-1})	TSS (mg L^{-1})	COD (mg L^{-1})	BOD_5 (mg L^{-1})	NTK (mg L^{-1})	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	PO_4^{2-} (mg L^{-1})
S1	Min	22.5	6.9	5.7	1.8	142	1,038	412.5	9.9	7.9	3.2	5.7
	Max	29.5	8.3	9.1	3.5	301	1,525	755	16.8	24.4	21.7	24.9
	Mean	26.2	7.2	7.3	1.7	215.5	1,180.4	522.3	11.4	16.4	10.8	12.6
S2	Min	16.5	7.9	5.6	1.8	14	59.5	19.6	2.1	2.1	1.5	1.1
	Max	27	8.1	9.0	4.9	38	131	40	22.7	12.2	23.3	25.1
	Mean	18.2	6.9	6.5	1.5	26.9	101.8	35	11.9	6.2	7.8	11.8
S3	Min	17	7.8	3.3	1.5	52	220.2	106.7	43.4	56.7	0.2	1.9
	Max	27	8	4.4	3.6	327	375	156.3	53.8	160	4.1	15.5
	Mean	21.4	7.7	3.8	1.6	176.1	291.4	134.2	48.4	125.1	2.1	11.1
S4	Min	17.9	7.6	21.7	1.6	167.3	977.5	456.5	60.6	29.7	2.3	2.2
	Max	27.5	8.1	24.5	3.8	622	2,725	1,060	96.7	87.2	5.3	24.2
	Mean	20.8	7.9	23.3	1.6	408.7	2,011.1	621.8	85.5	60.7	3.4	8.9
S5	Min	12.4	7.5	7.3	1.7	51	351.3	144	17.8	17.5	0.2	3.7
	Max	25	8.1	10.2	3.3	308.5	663	308	48	52.9	2.1	27.5
	Mean	19.4	7.7	8.6	1.5	202.7	503.6	198.4	27.4	31.5	1.1	9.6
S6	Min	14.5	7.7	3.8	1.6	27	386.5	35	4.9	1.1	1.1	0.5
	Max	23.5	8.2	4.5	3.3	92	689	178	22.8	17.4	28.1	12.1
	Mean	17.3	7.8	3.1	1.5	50.4	516.3	119.2	14.8	7.7	12.2	4.9
S7	Min	10.9	7.7	8.3	1.8	19.5	84	20	7.5	1.7	13.2	0.4
	Max	24	8.2	9.2	4.1	25	150	57.5	19.2	20	39.7	17.4
	Mean	19.3	7.9	8.7	1.9	27	94.5	41.4	12.7	5.9	26.6	7.1
S8	Min	10.5	7.6	4.3	0.6	61.3	342.6	145	0	26.4	0.5	1.8
	Max	24.5	7.9	6.3	3.5	183	544	360	57.7	65.4	21.5	37.9
	Mean	13.8	6.9	4.8	1.3	84.7	390.0	164.5	34.1	32.0	4.3	13.5
S9	Min	10.5	7.6	8	0.7	12	81.9	5	0	1.5	2.5	1.5
	Max	24.5	8.2	10.3	3.7	48	145	62.5	16.9	18.7	42.2	35.3
	Mean	12.2	7	6.6	1.3	21.2	97.2	23.2	10.0	4.8	16.2	13.8
S10	Min	11.5	7.6	5.6	0.7	56	352.1	75	9.5	29.1	0.1	0.6
	Max	24.5	7.9	8.9	3.3	155	635	186	15	73.6	1.0	14.4
	Mean	13.2	6.9	4.8	1.3	65.7	444.8	99.5	7.9	28	0.6	5.5
S11	Min	15	7.5	5.7	1.7	34	252.3	40	11.2	21.7	0.4	2.1
	Max	24.5	8.1	7.4	3.3	89	391.5	174	23.3	35.8	12.7	20.6
	Mean	18.3	7.8	6.3	1.5	58.5	301.2	99.2	19.0	25.9	7.4	8.5
S12	Min	15	7.7	5.5	1.7	41	172.9	67.5	12.3	20.8	0.1	2.6
	Max	24.5	8	6.6	3.3	81	362	128	20	107	19.9	12.8
	Mean	18.1	7.8	6.2	1.5	65.3	229.4	90	16.0	38.4	8.4	6.6
S13	Min	15	7.7	5.6	1.7	30	192	100.3	10.7	20.7	1.6	2.7
	Max	26	8.2	6.3	3.4	75	298.5	178	23	107	11.4	12.2
	Mean	18.5	8.00	6.1	1.7	62.9	216.6	123	16.5	36.8	6.2	6.7
Tunisian standards (TN-106-02)		25	6.5 < pH < 8.5	–	–	30	90	30	1	1	50	0.05

chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum action's (ions that carry a positive charge). Organic compounds like oil, phenol, alcohol, and sugar have a low conductivity when in water. Conductivity is also affected by temperature: the warmer the water, the higher the conductivity. Studies of fresh water indicate that streams supporting good mixed fisheries have a range between 150 and 500 μS/cm. Conductivity outside this range could indicate that the water is not suitable for certain species of fish or macroinvertebrates. Industrial wastewater can range as high as 10,000 μS/cm [31]. Range of conductivity preferred for irrigation water should be less than 250 μS/cm [32]. In the present investigation, the EC mean values ranged from 3.1 mS/Cm for samples collected from the Bridge over Wadi Maleh before Wadi El Bey site (S6) to 23.3 mS/cm for discharge of Grombalia Tannery site (S4). A comparison with the earlier report by Khadhar et al. [14] on the same study site showed some similarities with a minimum EC of 2.35 mS/cm obtained at site (R3) and a maximum EC of 15,05 mS/cm obtained at an industrial site (R4) in their study.

3.1.1.5. Total suspended solid. TSS content of water depends on the amount of suspended particles, soil, and silt and is directly related to turbidity of water. Disposal of sewage and industrial effluents contributes suspended matter to river. The Tunisian Standard Institution has specified a maximum limit of 30 mg L^{-1} for TSS [23]. The present study showed that the measured TSS values were high with the exception of the sites S9 and S2 characterized by TSS mean values of 21.2 and 26.9 mg L^{-1}, respectively (Table 3). However, TSS recorded highest values at sites S4 (Discharge of Grombalia Tannery), S1 (Discharge of Grombalia Industrial area), and S5 (Bridge over Wadi El Bey) with mean values of about 408.7, 215.5, and 202.6 mg L^{-1}, respectively. The obtained results were compared with earlier studies and showed some similarities. Khadhar et al. [14] observed similar results with high suspended solids values at different discharge point of Wadi El Bey river with TSS values fluctuated between 242.5 mg L^{-1} for WWTP discharges site (R2) and 446 mg L^{-1} for industrial discharges site (OR4) [14]. Rassam et al. [30] observed high suspended solids at waste discharge point of Oujda river—Morocco with TSS values fluctuated between 403 and 988 mg L^{-1}. Makhoukh et al. [33] observed high TSS values for Wadi Moulouya water (Morocco) varying between 123 and 2,730 mg L^{-1}. Finally, Mouni et al. [34] observed that TSS values in Wadi Soummam (Algeria) ranged between 5 and 198.6 mg L^{-1}.

3.1.1.6. Chemical oxygen demand. COD is the amount of oxygen used to oxidize chemical substances through chemical processes. The estimation of COD is of great importance for water having unfavorable conditions for the growth of micro-organisms, such as presence of toxic chemicals. Analyzed samples for COD in Wadi El Bey river water were mean values ranging between a minimum of 94.5 mg L^{-1} for S7 (Agricultural drainage—Wadi Maleh) and a maximum of 2,011 mg L^{-1} for S4 (Discharge of Grombalia Tannery). Tunisian Standard's tolerable limit is of 90 mg L^{-1} [23]. According to this, all the study sample sites were unsafe for use because COD values were almost higher than the acceptable limit. The highest COD levels were registered at sites S4 (Discharge of Grombalia Tannery) and S1 (Discharge of Grombalia industrial area) with mean values of about 2,011 and 1,180 mg L^{-1}, respectively. These results can be attributed to the high organic content of industrial effluents and insufficiently treated effluents discharged into the Wadi.

The determination of 5-d BOD_5 is the standardized experimental procedure to determine the relative oxygen requirements for aqueous microbes to consume organic materials in wastewater, wastewater treatment plant (WWTP) effluents, or surface water [35]. BOD_5 has been used as an indicator for organic pollutants in most aquatic systems, especially a good indicator for biodegradable organic compounds [36]. The Tunisian Standard Institution has specified a maximum limit of 30 mg L^{-1} for biological oxygen demand (BOD_5) [23].

The present study (Table 3) showed that with the exception of the site S9 (Agricultural drainage—Beni Khaled) characterized by a BOD_5 mean value of about 23.2 mg L^{-1}, all the other study sample sites are unsafe for use because BOD_5 values were almost higher than the acceptable limit. The highest BOD_5 levels were registered at sites S4 (Discharge of Grombalia Tannery) and S1 (Discharge of Grombalia industrial area) with mean values of about 621.8 and 522.3 mg L^{-1}, respectively. In fact, natural sources of BOD_5 in surface water include organic material from decaying plants and animal wastes. Human sources of BOD_5 include feces, urine, detergents, fats, oils, and grease, etc.

3.1.1.7. Phosphates and nitrates. Phosphates and nitrates are important parameters to assess the water quality. Photosynthesis and respiration play an important role in the self-purification of natural water. The disturbance of stationary state between photosynthesis and respiration leads to chemical and biological changes reflecting pollution. High levels of these species increase the growth of vegetation in water systems and increase the oxygen demand. The enrichment in nutrients and the enhancement of productivity and respiration lead to such imbalance. In the present investigation, the mean values of organic pollutants (NTK, NH_4^+, NO_3^-, and PO_4^{2-}) in the watershed of Wadi El Bey were recorded in Table 3.

3.1.1.8. Phosphate. Phosphate contamination comes from disposal of detergent contaminated sewage and directs clothes in water and use of fertilizer and pesticides. Total phosphate (TP) mean levels were present in high amount in all collected samples (Table 3). TP (PO_4^{2-}) mean level ranged from 4.9 mg L^{-1} (S6) to 13.8 mg L^{-1} (S9). The Tunisian standards for phosphate in effluent is fixed to 0.05 mg L^{-1} PO_4^{2-} [23]. This limit was always exceeded by at least 98 order of magnitude in all the water collected samples and would cause eutrophication in the river; especially in the Agricultural drainage—Beni Khaled site (S9; 13.8 mg L^{-1}) and the WWTP discharges—Beni Khaled site (S8; 13.5 mg L^{-1}). The high levels of TP indicate that the phosphate sources could be the fertilizer used on farms and/or wastewater contaminated with detergents discharged into the Wadi. The high levels also could be attributed to the decreased flux in the river due to seasonal variations.

3.1.1.9. Nitrate—ammonium. Agriculture has been recognized as the main anthropogenic source responsible for high nitrate-nitrogen content in groundwater [37,38]. In fact, the main sources of nitrogen compounds in water are fertilizers that mainly contain nitrate ion (NO_3^-), but also ammonium (NH_4^+), ammonia, urea, and amines. The most widely applied nitrogen fertilizers are probably $NaNO_3$ (sodium nitrate) and NH_4NO_3 (ammonium nitrate). The present study (Table 3) showed that the mean levels of nitrate (NO_3^-) concentration ranged from 0.6 mg L^{-1} for S10 sample to 26.6 mg L^{-1} for S7 sample. Nitrate concentration had the highest mean values of 26.6 and of 16.2 mg L^{-1} recorded at the Agricultural drainage—Wadi Maleh site (S7) and the Agricultural drainage—Béni Khaled site (S9), respectively. However, lower nitrate concentration value of about 0.6 mg L^{-1} was recorded at Wadi El Bey before WWTP discharges—Béni Khaled site (S10). The maximum values recorded at stations S7 and S9 proved the agricultural anthropogenic source that was responsible for high nitrate content in Wadi El Bey Water.

In the present investigation, the ammonium (NH_4^+) concentration mean levels ranged from 4.8 mg L^{-1} (S9) to 125 mg L^{-1} (S3). All NH_4^+ concentration levels were almost higher than the acceptable limit of 1 mg L^{-1} recommended by the Tunisian standard [23]. Ammonium concentration had the highest mean values of 125 and of 60 mg L^{-1} recorded for the Treated wastewater—WWTP Grombalia site (S3) and for the discharge of Grombalia Tannery site (S4), respectively. The high values of ammonium-nitrogen in water samples were probably due to the decomposition of proteins and nitrogen-rich compounds present in the organic waste discharge. However, lower ammonium concentration values of about 4.8 and 5.9 mg L^{-1} were recorded for Agricultural drainage—Béni Khaled site (S9) and for the Agricultural drainage—Wadi Maleh site (S7), respectively. In fact, the NH_4^+ concentrations in the Wadi presented an excellent indicator of water pollution caused by organic waste from agricultural, domestic, or industrial discharges.

The high nutrient values (phosphates and nitrates) could lead to the growth of blue-green algae, which could release toxic substances (cyanotoxins) into the water. Cyanotoxins are known to have caused the death of farm livestock [39].

3.1.2. Bacteriological study

The microbiological water quality of the 13 sampling sites all along the Wadi El Bey river was examined in this study twice per season during three years (2012–2014). This river receives discharges of contaminated water from storm water, combined sewer overflows, agricultural drainage, and incompletely disinfected urban and industrial wastewater. Frequent exceedance of Wadi El Bey microbiological water quality standards resulted in a health risk to the public who use the river water. Table 4 summarizes the results obtained on the monitoring of the water quality of Wadi El Bey. These reveal that the investigated water samples contained considerable numbers of *Fecal coliforms* (FC), *Fecal streptococci* (FS), *E. coli*, *Salmonella* (S), *Staphylococcus*, and *Pseudomonas*.

3.1.2.1. Fecal pollution. *E. coli* and *Fecal coliforms* are considered the best indicators for the assessment of fecal pollution and the presence of pathogenic bacteria, viruses, and parasites, in sewage and industrial effluents [40]. During the monitoring period, high fecal parameter concentrations (*Fecal coliform*, *E. coli* and *Streptococci*) were observed in the Wadi (Table 4).

3.1.2.2. Fecal coliforms. *Fecal coliforms* mean numbers ranged from 2.2×10^3 CFU/100 ml for Agricultural drainage—Wadi Maleh site (S7) to 265.3×10^3 CFU/100 ml for WWTP discharges—Béni Khaled site (S8). The concentration of *fecal coliforms* in Wadi El Bey river at all sites exceeded the recommended limit (2×10^3 CFU/100 mL) by the Tunisian standards

Table 4
Summary of microbiological analyses on water samples of Wadi El Bey

		Fecal coliforms (10^3 CFU/100 mL)	*Fecal streptococci* (10^3 CFU/100 mL)	*E. Coli* (10^3 CFU/100 mL)	*Staphylococcus* ((CFU/100 mL)	*Salmonella* (CFU/5,000 mL)	*Pseudomonas* (CFU/100 mL)
S1	Min	13	12	8.5	0	0	0
	Max	289.3	104	15	155	500	75
	Mean	146	57.8	11.7	27.3	224.4	55.3
S2	Min	5	0	2	0	0	0
	Max	408.5	53	34	310	384	1,235
	Mean	113.2	22.5	8.9	91.1	164	180.3
S3	Min	4	10	2	58	220	10
	Max	273	395.5	17	71,000	638	500
	Mean	127.1	164.4	6.3	10,216	454.7	272.3
S4	Min	7	0	5	0	10	0
	Max	46	471	8	1,100	1,000	306.8
	Mean	32.6	12	5.2	272.3	333.3	156.4
S5	Min	13	14	5	55	0	0
	Max	485	125	12	16,000	400	300
	Mean	220	48.8	9.5	2,384.6	188.1	155.9
S6	Min	6	5.5	5	0	0	0
	Max	470	11	14	600	116	10
	Mean	95.1	9.3	9.2	70.6	61	3.3
S7	Min	0.2	0	0.2	0	0	0
	Max	5	3	3.2	5	0	0
	Mean	2.2	1.8	2.4	1.4	0	0
S8	Min	22	0	11	5	0	100
	Max	722.5	555.5	100	99,000	738	840
	Mean	265.3	184.0	47.7	14,163	139	369.3
S9	Min	0.2	0	0.2	0	0	0
	Max	4.8	7	1.9	62	0	0
	Mean	2.4	1.2	1.7	18.6	0	0
S10	Min	6.8	5	3	0	0	0
	Max	73.5	555	12	480	269	0
	Mean	17.6	107.8	6.3	137.6	117.7	0
S11	Min	4.1	6	5	30	70	0
	Max	77	409	12	11,000	313	2,110
	Mean	34.4	80.7	7.9	1,626.4	188.4	310.4
S12	Min	8	6	4	0	60	0
	Max	51	409	12	200	385	180
	Mean	21.5	81.6	6.9	89.6	248.9	32.9
S13	Min	4	1	3	0	217	20
	Max	11	9	5	1,110	1,080	259
	Mean	7.3	6	5.5	127.4	307	154.3
Tunisian standards (TN-106-02)		2	1	Absence	Absence	Absence	Absence

(TN-106-02). It was evident that the main origin of these micro-organisms was the fecal matter discharged with wastewater effluents in the Wadi, these results were confirmed by Kolarevic et al. [41]. After each pollution source, there was a gradual decrease in *coliforms* values. This phenomenon was due to dilution of the discharge and self-purification of the Wadi.

3.1.2.3. E. coli. *E. coli*, the most widely adopted indicator of fecal pollution, was detected in all samples collected for this study. *E. coli* mean values ranged from 1.7×10^3 CFU/100 mL for Agricultural drainage—Béni Khaled site (S9) to 47.7×10^3 CFU/100 mL for WWTP discharges—Béni Khaled site (S8) (Table 4). The concentration of *E. coli* in Wadi El Bey river at all sites exceeded the recommended limit (absence) by the Tunisian standards [23]. The Wadi El Bey river was highly polluted, despite being quite a popular place in Tunisia.

The mean concentration of *fecal streptococci* in the Wadi El Bey stream was ranged from 1.8×10^3 CFU/100 ml for Agricultural drainage—Wadi Maleh site (S7) to 184×10^3 CFU/100 ml for WWTP discharges—Béni Khaled site (S8) exceeding Tunisian standards (1×10^3 CFU/100 mL). These values remained higher than those reported by other works [42–44].

According to the fecal pollution analysis, Wadi El Bey river presented a poor water quality because of the strong fecal pollution (>1,000 CFU/100 ml) [23].

The higher *fecal coliforms*, *Streptococci*, and *E. coli* counts measured is related to high concentration of physicochemical parameters and can be attributed to the high contaminate domestic and industrial wastewaters directly discharged into the Wadi. Nougang et al. working on the abundance of *fecal coliforms* and *E. coli* in ground water in the coastal area of Cameroon (Central Africa) obtained similar results [45] and confirmed by other study conducted on Minho/Miño river (Portugal/Spain) [46].

3.1.2.4. Staphylococcus. In the study area, *Staphylococcus* mean concentration ranged from 1.4 CFU/100 ml for Agricultural drainage—Wadi Maleh site (S7) to 14163 CFU/100 ml for WWTP discharges—Béni Khaled site (S8), exceeding Tunisian standards. The high level of *Staphylococcus* at the site S8 can be mainly attributed to the great amount of raw or not properly treated wastewater of Beni Khaled WWTP. The presence of *Staphylococcus* in almost all water samples should be considered an alarming factor and indicated that this water was not safe for users; *Staphylococcus* are opportunistic bacteria responsible for nosocomial infections. It is eliminated in the feces and disperses in the external environment (soil, water), where they do not survive very long [47].

3.1.2.5. Salmonella. *Salmonella Shigella* is one of the most important pathogens involved in human food-borne illness [48]. In the present investigation, Table 4 showed that *Salmonella* was absent in the Agricultural drainage—Wadi Maleh site (S7) and in the Agricultural drainage—Béni Khaled site (S9). Nevertheless, outside these two sites (S7 and S9), *Salmonella* was detected in all the other sites with mean values ranged from 61 CFU/100 mL at Bridge over Wadi Maleh before Wadi El Bey site (S6) to 454 CFU/100 mL at Treated wastewater—WWTP Grombalia site (S3), exceeding the recommended limit (absence) by the Tunisian standards [23]. Typhoid fever is caused by *Salmonella typhi*. Consequently, the potential health risk posed by the consumption of water from the Wadi El Bey river by rural residents and consumers in the Grombalia region must not be underestimated.

3.1.2.6. Pseudomonas. *Pseudomonas* can, in rare circumstances, cause community-acquired pneumonias as well as ventilator-associated pneumonias, being one of the most common agents isolated in several studies [49]. In the study area, *Pseudomonas* was absent in the agricultural drainage—Wadi Maleh site (S7), in the Agricultural drainage—Béni Khaled site (S9) and in the Wadi El Bey before WWTP discharges—Béni Khaled site (S10). Nevertheless, outside these three sites (S7, S9, and S10), *Pseudomonas* was detected in all the other sites with mean values ranged from 32.9 CFU/100 mL at Bridge over Wadi El Bey—Soliman city site (S12) to 369 CFU /100 mL at WWTP discharges—Béni Khaled site (S8), exceeding the recommended limit (absence) by the Tunisian standards [23]. The presence of this species indicated that the water samples were probably contaminated with human and animal feces [50]. The higher *Pseudomonas* counts measured at WWTP discharges of Béni Khaled indicated a non-efficient purification.

The microbiological pollution detected at the 13 selected sites can be attributed mainly to a large amount of raw or improperly treated urban and industrial wastewater, while increased agricultural activity in this area during the sampling period probably contributed to the detected organic pollution. According to the results, it can be concluded that the microbial quality of the Wadi El Bey water was poor and unacceptable for human consumption due to fecal pollution and the pathogenic bacteria. This indicated the potential risk of infection for consumers and calls for prompt intervention to mitigate the socioeconomic and health impact of water-borne diseases in these rural communities.

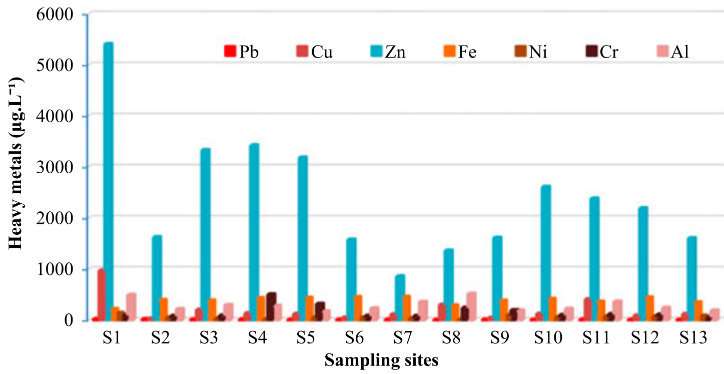

Fig. 2. Mean concentrations of heavy metals in the water samples at each site in Wadi El Bey river during 2012–2015.

3.1.3. Heavy metals pollution study

The heavy metals (Pb, Cu, Zn, Fe, Ni, Cr, and Al) water quality of 13 monitoring sampling sites along the Wadi El Bey river was examined in this study twice per season for 3 years (2012–2014). Fig. 2 summarizes the obtained heavy metals mean levels.

Results showed that Pb, Cu, Zn, Fe, Ni, Cr, and Al were detected in all water samples analyzed in this study and have the maximum contaminant levels of 13.2 µg L^{-1} (S1), 965 µg L^{-1} (S1), 3,989 µg L^{-1} (S1), 448 µg L^{-1} (S7), 133 µg L^{-1} (S1), 496 µg L^{-1} (S4), and 506 µg L^{-1} (S8), respectively (Fig. 2). These findings were higher than reported in literature on the same river [14].

In the present investigation, among the seven heavy metals analyzed, Zn was the most abundant all along the Wadi El Bey river with minimum mean level of 847 µg L^{-1} at site S7 (Agricultural drainage—Wadi Maleh) and maximum mean level of about 5,399 µg L^{-1} at site S1 (Discharge of Grombalia industrial area). This result is due to the presence of the Zn in natural water [51].

Otherwise, mean levels of Cu range from 21 µg L^{-1} at site S2 (Discharge of beer industry SONOBRA—Grombalia) to 965 µg L^{-1} at site S1 (Discharge of Grombalia industrial area). Furthermore, results showed that the concentrations of Pb, Fe, Ni, Cr, and Al were of about 100 µg L^{-1}, 1,000 µg L^{-1}, 200 µg L^{-1}, 500 µg L^{-1}, and 5,000 µg L^{-1}, respectively. They were within the allowed Tunisian limits for all sites in the study area [23]. However, the concentration of Zn and Cu were found to be higher than the allowed Tunisian limits (5,000 and 500 µg L^{-1}, respectively) in, respectively, 8 and 48% only for the Discharge of Grombalia industrial area (S1) water samples analyzed in this study. The excess heavy metal load of Wadi El Bey river water could be attributed to the discharge of industrial effluents and municipal wastes, geology of the river and catchment area. Though some of the detected heavy metals were beneficial for human and plants up to a certain limit, it may be harmful beyond that. Adoption of adequate measures to remove the heavy metal load from the industrial wastewater and renovation of sewage and industrial treatment plants discharged on Wadi El Bey river were suggested avoiding further deterioration of the river water quality.

3.2. Coagulation/Flocculation treatment

3.2.1. Efficiency of the coagulation/flocculation method for the treatment of industrial effluents

In order to develop a sustainable management model and to limit the pollution of the Wadi El Bey river resulting from the industrial wastewater of Grombalia area (S1), several coagulation/flocculation (CF) experiments were conducted.

According to the Tunisian standards, mean values of COD, BOD_5, TSS, NTK, NH_4^+, PO_4^{2-}, Cu, and Zn in the samples analyzed from industrial effluent (S1) discharged in the Wadi were much higher than the permissible levels (Tables 3 and 4 and Fig. 2). In order to determine the optimal CF conditions, a series of standard jar tests were conducted evaluating coagulant nature and doses that mostly affect the process efficiency.

The efficiency of CF treatment was evaluated measuring the organic matter removal (COD) and the decolorization rates since the Discharge of Grombalia industrial area (S1) were mainly composed of textile wastewater with high COD content and a strong coloration due to the presence of dyes. A series of CF experiments were conducted using six chemical coagulants: lime slurry ($CaCO_3$), aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and ferrous sulfate ($FeSO_4$). Two flocculants were tested for their

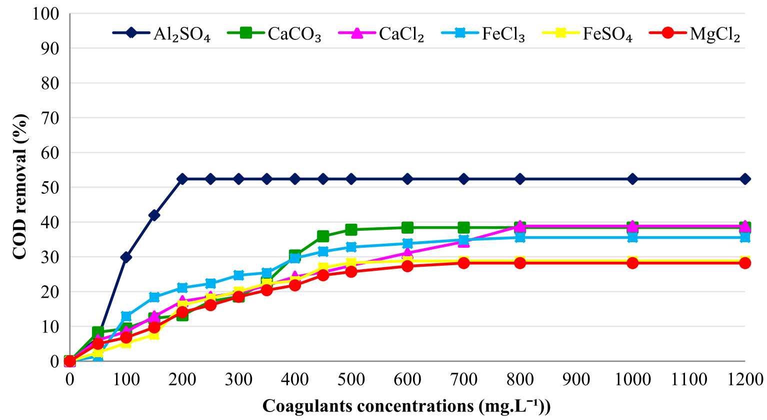

Fig. 3. Percentage of COD removal as a function of different coagulant dosage.

clarification capabilities: polyacrylamide and CHT-flocculant. Fig. 3 presented the efficiency of COD removal according to the different coagulants tested.

Alum was found to be generally superior to the other coagulants in removing COD. The results indicated that the use of 200 mg L^{-1} of alum reduced the COD by a value of 52.4% with a pH decreased from 7 to 6.37. Any increase in alum dosage beyond 200 mg L^{-1} did not result in significant COD removal. Similar results on textile effluents have been achieved in different studies that used alum as a coagulant [52,53]. The removal of COD was mainly attributed by the formation of precipitates from the combination of the soluble organics and the coagulant [54]. Basic reaction occurred during coagulation process using alum is shown by the following equation:

$$Al_2(SO_4)_3 + 6HCO_3^- \leftrightarrow 2Al(OH)_3(\downarrow) + 3(SO_4)^{2-} + 6CO_2 \quad (3)$$

The influence of coagulant nature and dosage on the color removal was presented in Fig. 4. It can be clearly seen that alum has performed better than the other coagulants, especially in removing color from wastewater. Decolorization rate increased to reach 67.5% at alum concentration of 200 mg L^{-1} with a pH decreased to 6.37. The results were in agreement with the findings of other workers [18,52,53]. Any increase in alum dosage beyond 200 mg L^{-1} did not result in significant color removal.

Nevertheless, throughout the experiments (Figs. 3 and 4), as the coagulant concentration raised, a gradual pH decrease was observed between 6.9 and 4.2. The acidic character of coagulant can explain the decrease in pH (Al^{3+}) used [55]. When reacting with OH^- ions of wastewater, aluminum will precipitate in the form of $Al(OH)_3$ [56]. According to Stephenson and Duff. [57], the influence of pH on chemical CF may be considered a balance of two competitive forces: (1) between H^+ and metal hydrolysis products

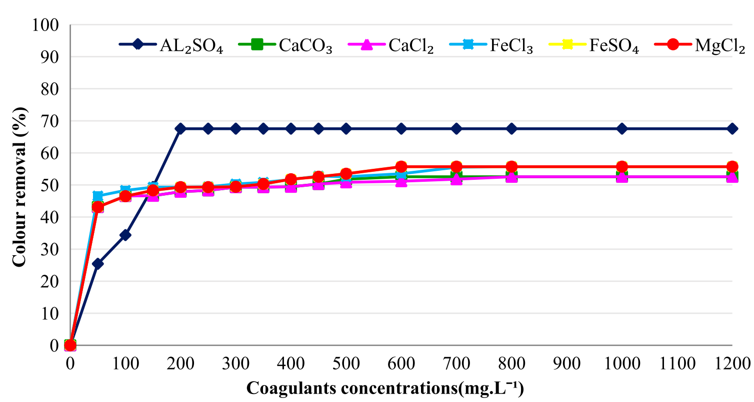

Fig. 4. Decolorization rates as a function of different coagulant dosage.

for interaction with organic ligands and (2) between hydroxide ions and organic anions for interaction with metal hydrolysis products.

The aim of this first run was to determine the optimum coagulant dosage required for COD and color removal. Alum was found to be generally better than the other coagulants, especially in removing COD as well as color from wastewater. Any changes in COD and color removal were observed for alum dosages higher than 200 mg L^{-1}; therefore, 200 mg L^{-1} was selected as the optimum alum dosage for the remainder of the study.

The coagulation efficiency of wastewater can be improved by the use of flocculants [58,59]. Flocculation occurs when solid particles aggregate into large, but loose particles resulting from the interaction of the flocculants with the surface charge of the suspended solid and subsequent coalescing of these aggregates into large floc that settle out of suspension [60]. This process has been extensively used in the industry to remove suspended solids such as clarification of wastewater treatment [61], clarification of drinking water, color removal in paper making industry, and mineral processing [62].

In the present investigation, flocculation process has been applied using two polyelectrolyte flocculants: polyacrylamide and CHT-flocculant (Figs. 5 and 6). In all cases, flocculation efficiency was increased gradually with flocculants dosage reaching the maximum levels at flocculants (polyacrylamide and CHT-flocculant) concentrations of 50 mg L^{-1}. The results were in agreement with the findings of other workers [18]. Any increase in flocculant dosage beyond 50 mg L^{-1} did not result in significant COD and color removals. On the other hand, it can be clearly seen that CHT-flocculant has performed better than the polyacrylamide in removing color and COD from wastewater. Khouni et al. [18] reported similar results for textile wastewater. The maximum flocculation efficiency obtained using alum at a concentration of200 mg L^{-1} and CHT-flocculant at a concentration of 50 mg L^{-1} was about 99 and 77.8% for decolorization and COD removal, respectively (Figs. 5 and 6). Khouni et al. [18] have reported also that the combination of alum and

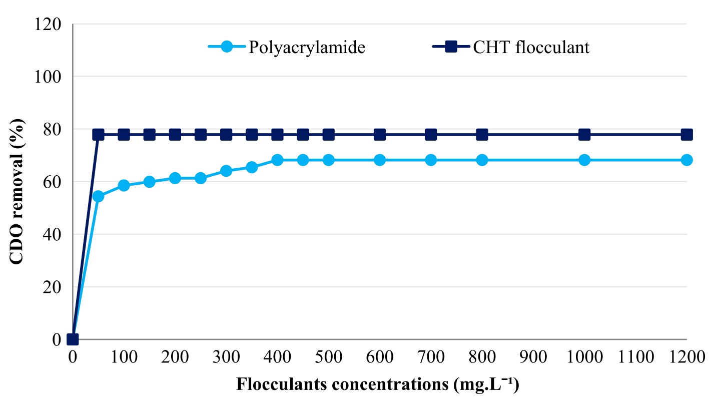

Fig. 5. Effect of flocculant dosage on COD removal.

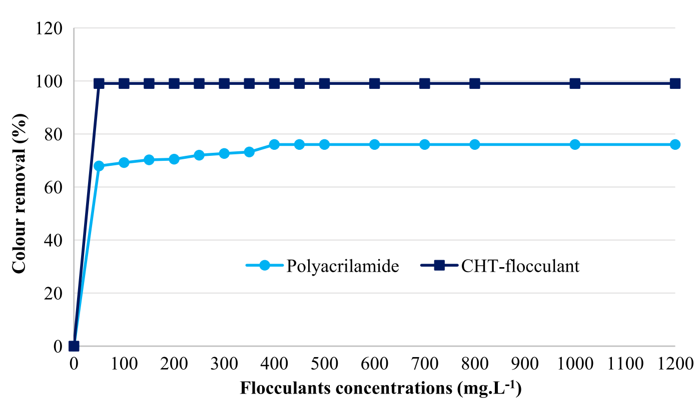

Fig. 6. Effect of flocculant dosage on color removal.

CHT-flocculant gave the best result for maximum textile wastewater treatment.

3.2.2. Optimization of CF process using RSM approach

Preliminary experiments were carried out to screen the appropriate parameters and to determine the experimental domain. The experimental results by application of jar test indicated that the use of alum as coagulant (200 mg L^{-1}) combined with the CHT-Flocculant (50 mg L^{-1}) appeared to be the appropriate choice with the highest COD and color removal efficiency and the least coagulant and flocculant consumption.

The effects of coagulant concentration (*X*1), flocculant dosage (*X*2), and initial solution pH (*X*3) were investigated on three responses: COD removal (*Y*1), decolorization efficiency (*Y*2), and final pH (*Y*3). Table 5 showed the coded experiments conducted according to experimental design along with the response values.

The statistical analysis of CCD experimental results, response surface modeling, and optimization of process variables were carried out using NemrodW software. The statistical analysis employed Fisher's "*F*" test and Student's "*t*" test were registered at Tables 6 and 7. In general, the larger magnitude of "*t*" and the smaller value of "*p*", more significant is the corresponding coefficient term [18].

According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant.

At the end of the coagulation process, the final empirical models in terms of coded factors after excluding the insignificant terms for COD removal (*Y*1), decolorization rates (*Y*2), and final pH (*Y*3) of S1 effluent were obtained in Eqs. (3), (4), and (5), respectively:

Table 5
Experimental results of CCD designed experiments for CF treatment of wastewater collected from the discharge of Grombalia industrial area (S1)

	Factors			Responses		
Run no.	*X*1 (mg L^{-1})	*X*2 (mg L^{-1})	*X*3 (–)	*Y*1 (%)	*Y*2 (%)	*Y*3 (–)
1	125.00	25.00	7.00	55.89	79.21	6.87
2	125.00	25.00	7.00	55.80	79.38	6.89
3	275.00	25.00	7.00	61.03	83.16	6.13
4	275.00	25.00	7.00	61.10	83.25	6.17
5	125.00	75.00	7.00	57.82	85.80	6.70
6	125.00	75.00	7.00	57.84	85.78	6.73
7	275.00	75.00	7.00	87.87	99.82	6.17
8	275.00	75.00	7.00	87.80	99.78	6.11
9	125.00	50.00	5.00	49.69	74.52	4.84
10	125.00	50.00	5.00	49.72	74.49	4.83
11	275.00	50.00	5.00	69.38	89.53	4.95
12	275.00	50.00	5.00	69.39	89.56	4.95
13	125.00	50.00	9.00	64.71	76.29	7.39
14	125.00	50.00	9.00	64.62	76.35	7.32
15	275.00	50.00	9.00	74.37	99.30	7.25
16	275.00	50.00	9.00	74.42	99.25	7.24
17	200.00	25.00	5.00	68.24	77.22	4.27
18	200.00	25.00	5.00	68.25	77.24	4.24
19	200.00	75.00	5.00	69.73	86.68	4.03
20	200.00	75.00	5.00	69.69	86.65	4.04
21	200.00	25.00	9.00	74.69	79.38	7.47
22	200.00	25.00	9.00	74.65	79.53	7.41
23	200.00	75.00	9.00	77.23	99.32	7.11
24	200.00	75.00	9.00	77.18	99.40	7.08
25	200.00	50.00	7.00	77.80	99.10	6.25
26	200.00	50.00	7.00	77.80	99.10	6.25
27	200.00	50.00	7.00	77.80	99.10	6.28
28	200.00	50.00	7.00	77.80	99.10	6.28
29	200.00	50.00	7.00	77.80	99.10	6.25

Table 6
Estimated regression coefficient for CF treatment of wastewater collected from the discharge of Grombalia industrial area

R.C.	Coefficient value			F. Inflation			Standard deviation			"t" exp.			p-value		
	COD removal	Color removal	pH	COD removal	Color removal	pH	COD removal	Color removal	pH	COD removal	Color removal	pH	COD removal	Color removal	pH
$\alpha0$	77.800	99.100	6.262				0.015	0.022	0.011	5,208.41	4,514.47	570.75	***	***	***
$\alpha1$	8.079	6.989	−0.162	1.00	1.00	1.00	0.008	0.012	0.006	967.56	569.57	−26.49	***	***	***
$\alpha2$	4.094	6.554	−0.093	1.00	1.00	1.00	0.008	0.012	0.006	490.33	534.07	−15.08	***	***	***
$\alpha3$	4.236	3.308	1.383	1.00	1.00	1.00	0.008	0.012	0.006	507.32	269.58	225.41	***	***	***
$\alpha11$	−10.038	−6.422	0.300	1.03	1.03	1.03	0.013	0.019	0.009	−792.66	−345.07	32.21	***	***	***
$\alpha22$	−2.118	−5.656	−0.090	1.03	1.03	1.03	0.013	0.019	0.009	−167.26	−303.90	−9.72	***	***	***
$\alpha33$	−3.224	−7.767	−0.465	1.03	1.03	1.03	0.013	0.019	0.009	−254.61	−417.34	−50.03	***	***	***
$\alpha12$	6.196	2.525	0.039	1.00	1.00	1.00	0.012	0.017	0.009	524.70	145.50	4.47	***	***	***
$\alpha13$	−2.487	1.979	−0.056	1.00	1.00	1.00	0.012	0.017	0.009	−210.64	114.02	−6.49	***	***	***
$\alpha23$	0.268	2.617	−0.031	1.00	1.00	1.00	0.012	0.017	0.009	22.65	150.83	−3.60	***	***	**

Notes: R.C.: Regression Coefficient; *p*-value: the significance of the test; ***: extremely significant.

Table 7
Analysis of variance (NemrodW) for the fitted quadratic polynomial models of CF treatment of wastewater collected from the discharge of Grombalia industrial area (effect of coagulant concentration, flocculant concentration and pH)

		Sum of squares (SS)			Mean square (MS)			Ratio/$F_{statistics}$			p		
Sources of variation	Degree of freedom (DF)	COD removal (%)	Color removal (%)	pH (–)	COD removal (%)	Color removal (%)	pH (–)	COD removal (%)	Color removal (%)	pH (–)	COD removal (%)	Color removal (%)	pH (–)
Regression	9	2.68640E + 0003	2.52359E + 0003	33.6473	2.98489E + 0002	2.80399E + 0002	3.7386	26,7552.8033	11,6378.3004	6,211.5669	<0.01 ***	<0.01 ***	<0.01 ***
Residual	19	1.70825E + 0002	1.13403E + 0002	0.9879	8.99077E + 0000	5.96859E + 0000	0.0520						
Total	28	2.85722E + 0003	2.63699E + 0003	34.6352									

Notes: p-value: the significance of the test; ***: extremely significant; R^2 = 0.940 for COD removal ($Y1$); R^2 = 0.957 for decolorization ($Y2$); R^2 = 0.971 for final pH ($Y3$).

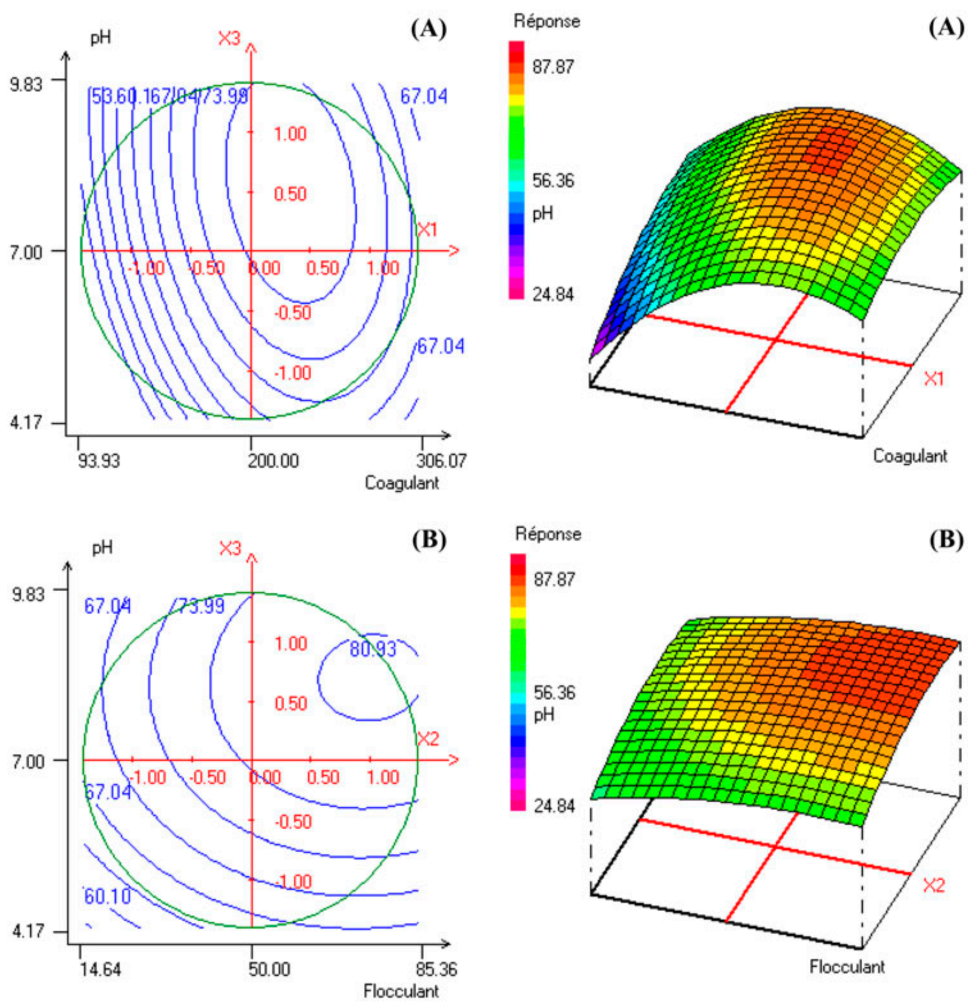

Fig. 7. Two-dimensional and three-dimensional response surface plots for the COD removal of industrial wastewater directly discharged in Wadi El Bey (S1) treated using CF treatment as a function of: (A) coagulant concentration and pH (flocculant concentration = 50 mg L^{-1}) and (B) flocculant concentration and pH (coagulant concentration = 200 mg L^{-1}).

$$Y_1 = 77.8 + 8.079\,X1 + 4.094\,X2 + 4.236\,X3 - 10.038\,(X1\,X1) - 2.118\,(X2\,X2) - 3.224\,(X3\,X3) + 6.196\,(X1\,X2) - 2.487\,(X1\,X3) + 0.268\,(X2\,X3) \quad (4)$$

$$Y_2 = 99.1 + 6.989\,X1 + 6.554\,X2 + 3.308\,X3 - 6.422(X1\,X1) - 5.656\,(X2\,X2) - 7.767\,(X3\,X3) + 2.525\,(X1\,X2) + 1.979\,(X1\,X3) + 2.617\,(X2\,X3) \quad (5)$$

$$Y_3 = 6.262 - 0.162 \times X1 - 0.093\,X2 + 1.383 \times X3 + 0.300 \times (X1\,X1) - 0.090 \times (X2\,X2) - 0.465 \times (X3\,X3) + 0.039 \times (X1\,X2) - 0.056 \times (X1\,X3) - 0.031 \times (X2\,X3) \quad (6)$$

Positive sign indicates synergistic effect, whereas negative sign indicates antagonistic effect [63]. The models developed were evaluated based on the correlation coefficient values. Coefficients with one factor represent the particular factor effect, while coefficients with two factors and those with second-order terms represent the interaction between the two factors and quadratic effect, respectively. For all models, analysis of variance (NemrodW) for COD removal (*Y*1), decolorization rates (*Y*2) and final pH (*Y*3) showed that fitted second-order response surface models were highly significant (Table 7).

The R^2-value of 0.940 for Eq. (4), of 0.957 for Eq. (5), and of 0.971 for Eq. (6) were considered relatively high indicating that there was a good agreement between the experimental and the predicted values uptake from the models. The regression coefficients

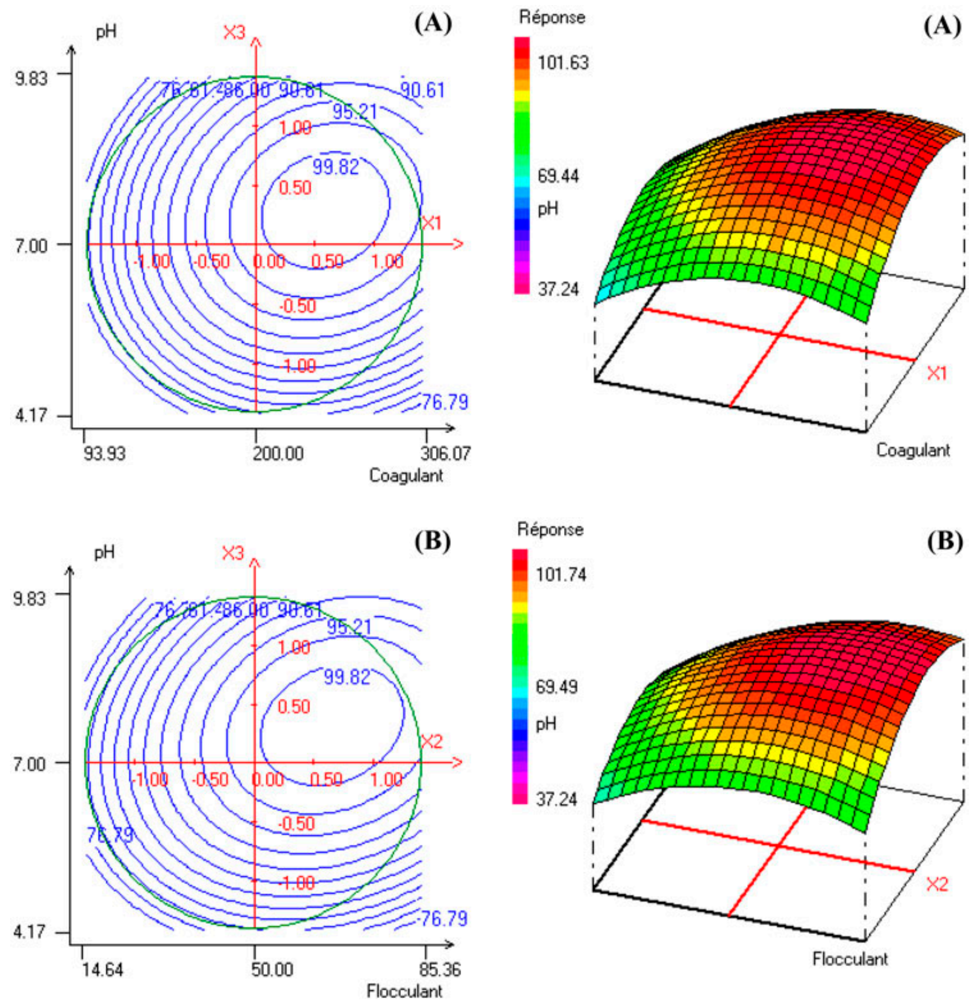

Fig. 8. Two- and three-dimensional response surface plots for the decolorization rates of industrial wastewater directly discharged in Wadi El Bey (S1) treated using CF treatment as a function of: (A) coagulant concentration and pH (flocculant concentration = 50 mg L^{-1}) and (B) flocculant concentration and pH (coagulant concentration = 200 mg L^{-1}).

and the interaction between each independent factor could be considered statistically significant for *p*-values below 0.01 with 99% of confidence interval. These results indicated that the accuracy of the polynomial models was well adapted.

Figs. 7 and 8 presented the two- and three-dimensional response surfaces, which were constructed to show the effects of the coagulant concentration, flocculant dosage, and the initial pH on the COD and color removal from industrial wastewater (S1: Discharge of Grombalia industrial area) using CF treatment. The graphs obtained showed the same behavior with the fluctuation of independent variables of coagulant concentration, pH, and flocculant concentration. For all experiments, the two- and three-dimensional (3D) surface plots showed the relative effects on COD removal and decolorization rates of any two variables when the remaining (third) variable was kept constant. Surface plots 7A and 8A showed the interactive effect on COD removal and decolorization, respectively, of coagulant concentration and pH by keeping flocculant concentration constant at 50 mg L^{-1}. Similarly, by keeping coagulant concentration constant at 200 mg L^{-1}, surface plots 7B and 8B showed the interactive effect on COD removal and decolorization of flocculant concentration and pH. The 2D and 3D surface plots showed that the best COD and color removal from industrial wastewater (S1: Discharge of Grombalia industrial area) were obtained at basic pH (Figs. 2 and 3). It was observed from the plots 7A and 7B that at pH higher to 6.5, the COD removal increased when pH increased. However, it was also

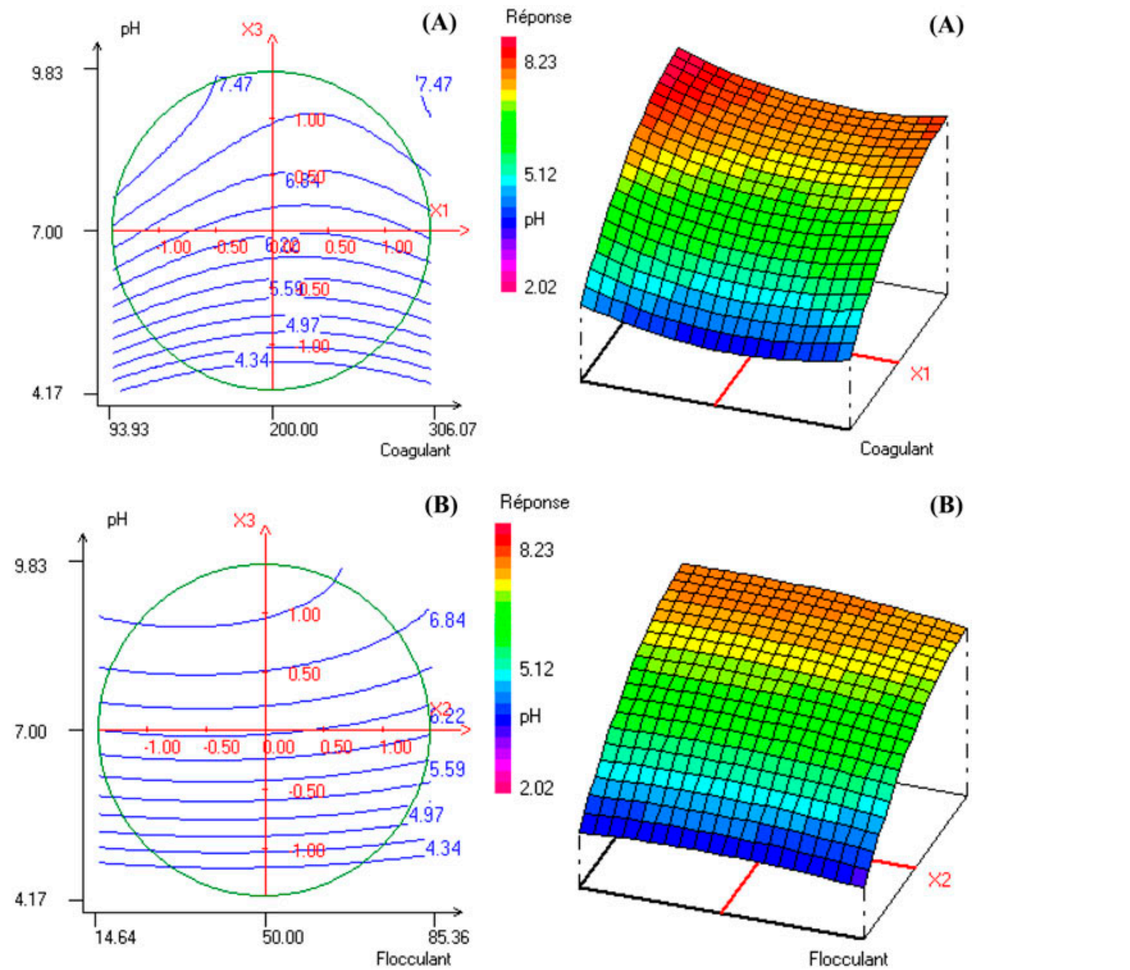

Fig. 9. Two- and three-dimensional response surface plots for final pH of industrial wastewater directly discharged in Wadi El Bey (S1) treated using CF treatment as a function of: (A) coagulant concentration and pH (flocculant concentration = 50 mg L^{-1}) and (B) flocculant concentration and pH (coagulant concentration = 200 mg L^{-1}).

observed from the plots 8A and 8B that at pH range between 7 and 8, the color removal increased when pH increased.

Results obtained above showed that pH affects decolorization and COD removal from the industrial wastewater (S1: Discharge of Grombalia industrial area) treated using CF treatment. This result agrees with similar observations reported in other studies [18].

With final pH as the response, the response surfaces (3D), and the contour plots (2D) of the quadratic model with one variable kept at central level and the other two varying within the experimental ranges were, respectively, shown in Fig. 9. The obvious through the response surfaces that the optimal conditions were exactly located inside the design boundary. The corresponding two-dimensional contours showed a considerable curvature in contour curves, implying that the three factors (coagulant concentration, flocculant dosage, and initial pH) were interdependent (Fig. 9). There were significant interactive effects on final pH between coagulant dosage and flocculant dosage (figure not shown), coagulant dosage and pH (Fig. 9(A)), as well as flocculant dosage and pH (Fig. 9(B)). Optimal COD removal (87.87%), decolorization rates (99.82%) and final pH solution (6.99) predicted from the models, occurred when the coagulant and flocculant concentrations were about 275 and 75 mg L^{-1}, respectively, at initial pH of 8.50. Graphical response surfaces were used to identify the optimum points. Satisfactory prediction equations were derived for COD and color removal using RSM to optimize the parameters.

A verification of the results using the set of optimized parameters was accomplished by performing the experiments incorporating the optimized variables.

Table 8
Physical and chemical characteristics of Grombalia industrial wastewater directly discharged in Wadi El Bey (S1) before and after CF treatment under optimal conditions

Parameter	Unit	Values before treatment	Values after treatment	Removal (%)	Tunisian standards (TN-106-02)
pH	–	7	6.9	–	6.5–8.5
TSS	$mg\ L^{-1}$	202	5.86	97.1	30
COD	$mg\ L^{-1}$	1,230	152.5	87.6	90
BOD_5	$mg\ L^{-1}$	600	90	85	30
NH_4^+	$mg\ L^{-1}$	21.5	0.34	98.4	1
NO_3^-	$mg\ L^{-1}$	1.5	0.24	83.6	50
PO_4^{2-}	$mg\ L^{-1}$	20.3	6.2	69.5	0.05
Pb	$\mu g\ L^{-1}$	<10	<10	–	100
Cu	$\mu g\ L^{-1}$	198	12	93.9	500
Zn	$\mu g\ L^{-1}$	1,160	182	84.3	5,000
Fe	$\mu g\ L^{-1}$	902	88	90.2	1,000
Ni	$\mu g\ L^{-1}$	266	156	41.4	200
Cr	$\mu g\ L^{-1}$	152	7.1	95.3	–
Al	$\mu g\ L^{-1}$	3,690	4,950	Increases	–

The experiments were conducted in triplicate. The average COD and color removal rates obtained through the experiments were about 87.6 and 99.9%, respectively, with neutral pH (pH 6, 9). These experimental findings were in close agreement with the model prediction.

Obtained results demonstrated the applicability of CF method for the treatment of industrial wastewater directly discharged in Wadi El Bey river (S1). The efficiency of CF treatment under optimal conditions in removing of organic matter, nutrients, and heavy metals from Grombalia industrial wastewater (S1) has been studied. The obtained results were presented in Table 8.

From the above results, it was obvious that a significant improvement in organic matter removal was obtained during CF under optimal conditions (Table 8) with maximum TSS, COD, and BOD_5 removals of about 97.1, 87.6, and 85%, respectively. Furthermore, results showed high efficiency in the decrease in nutrients during CF under optimal conditions with maximum NH_4^+, NO_3^- , and PO_4^{2-} removals of about 98.4, 83.6, and 69.5%, respectively. It should be noted the efficiency of the CF treatment in the effective removal of organic matter and nutrients. All parameters measured after CF treatment under optimal conditions were below the Tunisian Standards (NT 106–02), with the exception of COD (152.5 $mg\ L^{-1}$) and BOD_5 (90 $mg\ L^{-1}$) levels.

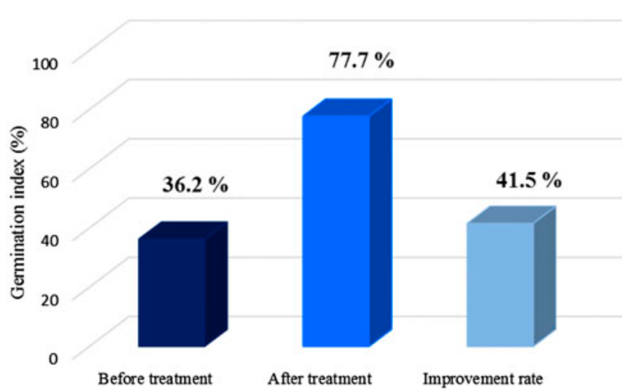

Fig. 10. GI (%) of *L. sativa* grown in industrial wastewater before and after CF treatment.

Regarding the heavy metals removal, it could be seen that during CF treatment, Cu, Zn, Fe, Ni, and Cr were broadly affected. Results showed high efficiency in the decrease in heavy metals during CF under optimal conditions with maximum Cu, Zn, Fe, Ni, and Cr removals of about 93.9, 84.3, 90.2, 41.4, and 95.3%, respectively. These heavy metals reached levels below the acceptable limits recommended by the Tunisian standard [23]. Otherwise, results indicated that the Pb was detected neither in the raw nor in the treated wastewater.

Nevertheless, when using alum, there were places to ensure that the residual content of Al in solution did not exceed 0.2 $mg\ L^{-1}$ (WHO standard). Following Table 8, CF treatment under optimal conditions with aluminum sulfate ($Al_2(SO_4)_3$) showed a high residual in aluminum. In fact, Al concentration was increased after CF treatment reaching 4.95 $mg\ L^{-1}$ (an increase of about 25.5%). Tang et al. [64] showed that the adding of alum ($Al_2(SO_4)_3$) as coagulant into treated solution will set off a series of complex chemical reactions which were known as dissolution, hydrolysis, and polymerization. Therefore, the Al concentration increased after CF treatment could be explained by these different reactions summarized on the following chemical reaction of aluminum sulfate in the water:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \leftrightarrows 2Al(OH)_3 + 3CaSO_4 + 6CO_2$$

Aluminum sulfate was commonly used as coagulant. Although effective for removing organic matter pollution, nutrients, and heavy metals, Al-based coagulants, particularly aluminum sulfate, may result in elevated concentrations of residual Al in finished water [65,66]. Residual aluminum in treated water was undesirable for esthetic reasons, but also because of a possible link between aluminum and adverse neurological effects such as Alzheimer's disease [67]. Therefore, special attention should be directed toward the use of biodegradable polymers (such as chitosan) in the CF treatment, which were more environmentally friendly.

3.3. Phytotoxicity study

The results of GI of *L. sativa* in two conditions of industrial wastewater, i.e. before and after coagulation/flocculation (CF) treatment were given in Fig. 10. As can be seen, GI values of *L. sativa* in raw Grombalia industrial wastewater (S1) was low revealing that raw industrial wastewater was significantly phytotoxic. Furthermore, the phytotoxicity reduced after CF treatment considering that GI of *L. sativa* values markedly increased. In this way, GI of *L. sativa* increased from 36.2% to about 77.7%. These results showed that CF process could effectively reduce toxicity of industrial wastewater for plants. Hence, this study provided evidence that CF treatment was a sustainable process for industrial wastewater and the treated effluent can be reused for irrigation purposes.

4. Conclusion

The Wadi El Bey river, located in the northeast part of Tunisia, is frequently used for different purposes. The appraisal of its water with respect to physicochemical and microbiological pollution is of immense significance for improving living standard and quality of life in this region. Therefore, monitoring of physicochemical and microbiological contamination on periodic basis should be an important component of the protection strategy in this area. The present study revealed the high level of the Wadi El Bey river pollution state. The concentration of different physicochemical and microbiological parameters was much beyond the permissible limit prescribed by WHO and by Tunisian standards (TN-106-02). Hence, direct use of untreated Wadi El Bey river water is at high risk for human health. In this study, the coagulation/flocculation (CF) process with aluminum sulfate ($Al_2(SO_4)_3$) as coagulant and CHT-flocculant was used for the treatment of Grombalia industrial wastewater directly discharged to Wadi El Bey river (S1). To maximize the removal of COD and color with neutral final pH, the jar tests were carried out in the experiments and RSM was applied to optimize the process. A CCD, i.e. a standard approach in RSM, was used to evaluate the effects and interactions of three factors, i.e. aluminum sulfate concentration, CHT-flocculant dosage and initial pH on the treatment efficiency. Results revealed that the maximum COD and color removal with final neutral pH could be achieved at optimal conditions, i.e. ($Al_2(SO_4)_3$) = 275 mg L^{-1}, CHT-flocculant = 75 mg L^{-1} and initial pH 8.50 from which the removal of COD and color were 87.87% and 99.82%, respectively, with final pH of 6.99. The study also showed that the regression equations could be used as the theoretical basis for industrial wastewater treatment using CF process.

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