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Optimization of coagulation–flocculation process in the treatment of surface water for a maximum dissolved organic matter removal using RSM approach

Sami Khettaf, Imen Khouni, Ghofrane Louhichi, Ahmed Ghrabi, Latifa Bousselmi, Kamel-Eddine Bouhidel and Mohammed Bouhelassa

ABSTRACT

The aim of this research work is the optimization of the coagulation/flocculation process in the treatment of surface water for maximum dissolved organic matter (DOM) removal using response surface methodology (RSM). For this purpose, several jar test experiments were performed in order to identify the most influencing factors. Afterwards, RSM was done to investigate the effects and the interactions of three chosen variables (coagulant concentration, flocculant concentration, and initial pH), whereas the responses were the DOM removal in terms of chemical oxygen demand (COD), in terms of absorbance at the wavelength 254 nm (UV-254), and the final pH. The optimal conditions were as follows: 133 mg/L of coagulant, 60 mg/L of flocculant and an initial pH equal to 6.91. Under these conditions, the efficiency removals were 56% in terms of COD and 59% in terms of UV-254 with a final pH equal to 6.78. High variance coefficient R^2 values, with 0.96 for the removal in terms of COD and 0.92 in terms of UV-254, confirm the reliability and the validity of the obtained model.

Key words | Box–Behnken design, coagulation/flocculation treatment, dissolved organic matter removal, optimization, response surface methodology, surface water

Sami Khettaf (corresponding author)
Kamel-Eddine Bouhidel
Laboratory of Chemistry and Environmental Chemistry LCEE, Department of Chemistry, Faculty of Material Sciences,
University of Batna 1,
Batna 05400,
Algeria
E-mail: *sami.khettaf@univ-batna.dz*

Imen Khouni
Ghofrane Louhichi
Ahmed Ghrabi
Latifa Bousselmi
Laboratory of Wastewater and Environment,
Water Research and Technologies Centre (CERTE),
Technopark Borj Cedria,
BP 273-8020,
Soliman,
Tunisia

Mohammed Bouhelassa
Environmental Process Engineering Laboratory,
University of Constantine 03,
Constantine 25000,
Algeria

HIGHLIGHTS

- Coagulation/flocculation is a very efficient process for removing dissolved organic matter from surface waters.
- Response surface methodology approach is a very effective and powerful tool for optimizing the coagulation/flocculation process.
- Optimization of the coagulation/flocculation process reduces the use of chemicals and protects the environment.

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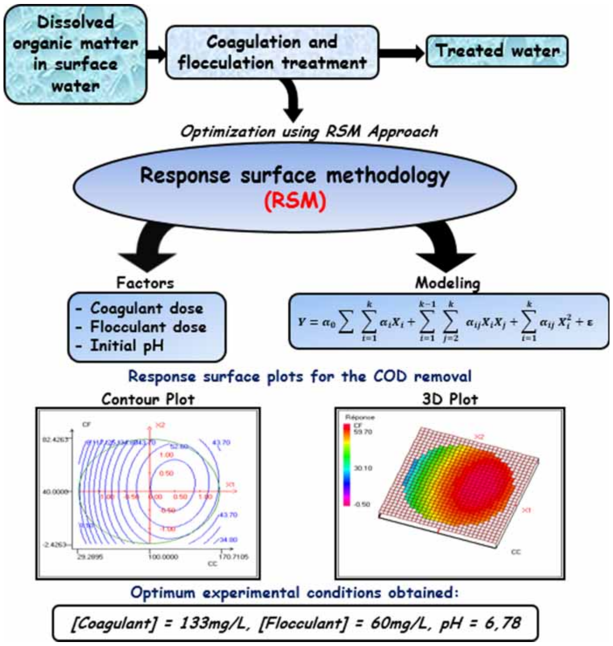
GRAPHICAL ABSTRACT



ACRONYMS AND ABBREVIATIONS

BBD	Box–Behnken design
CCD	Central composite design
CF	Coagulation/flocculation
COD	Chemical oxygen demand
DOM	Dissolved organic matter
NOM	Natural organic matter
RSM	Response surface methodology
UV-254	Absorbance at the wavelength 254 nm

INTRODUCTION

Drinking water production in a scenario where the contamination of aquatic environments is increasing has become a subject of global interest (Feihrmann *et al.* 2017; Khouni *et al.* 2020). In fact, the availability of fresh water is one of the most basic necessities of life, and this is what makes it one of the biggest global challenges while worldwide there are about 1.2 billion people who do not have access to potable water and more than six million children die as a result of waterborne diseases each year (Ali *et al.* 2010; Jain 2012; Palansooriya *et al.* 2020).

Traditionally, to balance between water supplies and water demand for humans, natural water resources such as rainwater, surface freshwater run-off, catchment and groundwater reservoirs have been used in this case. However, the quality of natural waters has suffered serious deterioration, especially surface water (lakes, rivers, dams …), and the main cause of this degradation is the excessive increase of dissolved organic matter, the emergence of new pollutants (trihalomethanes, pesticides …), etc. (Khettaf *et al.* 2016; Shen *et al.* 2020). Natural dissolved organic matter (DOM) is present in all natural waters (Liu *et al.* 2019). It is a heterogeneous complex mixture of various organic compounds varying in molecular size, structure, and chemical composition (Dulaquais *et al.* 2018; Hincapié-Upegui *et al.* 2020). It consists of various compounds including proteins, lipids, carboxylic acids, polysaccharides, amino acids, hydrocarbons and humic and fulvic substances (Wang *et al.* 2009; Mostofa *et al.* 2013).

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Many studies have proven that the chlorination of water intended for public consumption, in the presence of DOM, leads to the formation of disinfection by-products such as trihalogenethanes, and carcinogenic and toxic organic compounds (Ghernaout & Elboughdiri 2020; Jiang *et al.* 2020). Furthermore, the presence of DOM can be the cause of many other problems such as taste, odour, colors, biofilms, metal complexes, membrane fouling, high consumption of chemicals …etc. (Vepsäläinen *et al.* 2009; Mostofa *et al.* 2013). For all these reasons, the elimination of DOM or at least its reduction to an acceptable level is an imperative process that must be done to protect the health of consumers by producing drinking water that meets water quality standards and to avoid any problems that may be caused by their presence.

The Timgad dam (NE Algeria) is a reservoir dam used mainly to produce drinking water for one million inhabitants of the city of Batna (Amrane & Bouhidel 2019). As all surface water, the main sources of the DOM in this dam are the effluents of domestic wastewater after treatment (biological wastewater treatment) and domestic sewage along with excreta by human beings and various animals, which are directly or indirectly discharged into the watershed of the dam.

The plant of this dam uses a conventional treatment based on the use of the coagulation/flocculation (CF) technique, since it has been widely used for the treatment of surface water due to its several advantages such as the removal of organic, suspended and colloidal matters. It can also be effective in removing many protozoa, bacteria and viruses, it has been found to be cost-effective and easy to operate, and it is an energy-saving treatment alternative (Mhamdi *et al.* 2016; Feihrmann *et al.* 2017).

Generally, CF treatment is influenced by several parameters, such as coagulant and flocculant nature and concentrations, pH, temperature, etc. (Hussain *et al.* 2019). Therefore, finding the optimum value for these factors can improve the effectiveness of treatment.

Often, using traditional optimization, the optimal value for each variable is carried out by changing one factor while keeping all other factors constant. The problem with this method is that it takes a long time and that it is incapable of studying the effect of the interactions between the studied variables. This means this method is considered ineffective for determining the real optimal conditions. In order to find a solution to these deficiencies in the traditional method, the optimum values for the variables are determined using response surface methodology (RSM) (Mhamdi *et al.* 2016; Louhıchı *et al.* 2019).

In fact, RSM is a very useful tool, and a widely used technique for many treatment process optimizations. It is based on a group of mathematical and statistical methods in order to build a model of complex systems that makes it possible to evaluate the effects between the studied variables and to determine the optimal conditions which give the best possible processing performance and to predict the responses (Adlan *et al.* 2011; Guvenc *et al.* 2017).

The advantages of this method compared with the traditional method are that (i) it does not require a large number of experiences, (ii) it allows the studying of many variables at the same time and (iii) it makes it possible to study the interactions between the variables precisely and in a short time (Khouni *et al.* 2011).

Within this framework, this research work aims to enhance the performance of Timgad's treatment plant and to determinate the optimal operating conditions in order to obtain the best treatment performance in particular for the removal of dissolved organic matter from Timgad dam water by the CF treatment using RSM.

To the best of our knowledge, no study has so far been reported on the optimization of the CF process used on Timgad's treatment plant using RSM.

MATERIALS AND METHODS

Study area

The studied water samples were taken from the Timgad dam (NE Algeria). It is a recent dam built in 1994 and started in service in 2005. It is located 7 km northeast of Timgad and 35 km from the city of Batna in Algeria (Figure 1). It is a reservoir dam that mobilizes the surface waters of the Wadi Reboa with a surface area of 59,000 m^2 and a total capacity of 69 million m^3. The region of the studied dam is characterized by a semi-arid Mediterranean climate, with an annual precipitation average value of 357 mm. The treated water of this dam is used mainly to supply drinking

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Figure 1 | Geo-location of the Timgad dam in Algeria.

water to one million inhabitants of the city of Batna (Amrane & Bouhidel 2019).

Analytical methods

The water samples used in this investigation were obtained from the Timgad dam in Algeria. Their physicochemical characteristics were investigated in order to measure their level of pollution before and after the treatment process. Physicochemical analysis of water samples was conducted based on the analytical methods recommended by *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). The efficiency of the CF experiments was determined by measuring the amount of organic matter in samples before and after the treatment.

Regarding the fact that Timgad dam water contains a very low level of inorganic compounds (Tiri *et al.* 2016, 2017; Amrane & Bouhidel 2019), we suggested that Chemical Oxygen Demand (COD) concentration was attributable essentially to the organic matter content. Thus, in this investigation, DOM was evaluated in terms of COD. COD, which is considered as one of the most standardized methods for natural water as well as for wastewater, was measured using WTW™ Chemical Oxygen Demand Test Kits. The COD measurement was elaborated on the dissolved fraction organic matter of the water sample obtained after filtration using a Whatman GF/C glass-fiber filter with a pore size of 0.45 μm. The COD was conducted according to the American Public Health Association standard method (APHA 1998), which is based on the principal of the

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chemical oxidation of organic matter using an oxidant ($K_2Cr_2O_7$) under an extremely acidic condition and in the presence of a catalyst (silver sulfate) and mercury sulfate (recommended in order to avoid interference from the additional oxidation of Cl^- and formation of Cl_2 gas). The mixture was heated for at least two hours at 150 °C ±2 °C using a normalized thermoreactor (reference ECO 16 Velp scientifica Ref F10100126), and the COD concentration was measured using a UV-visible spectrophotometer type Perkin Elmer at a wavelength of about 420 nm (Rodier et al. 2009).

In this study, the measurement of UV-254 was also used as a parameter to monitor the DOM amount before and after each treatment applying the CF process. UV-254 absorbance has been reported as a simple and reliable parameter used for real-time monitoring and control of DOM removal in many treatment processes, and it has also been reported that it can be used as a useful parameter to represent the aromatic character of the organic compounds present in water samples (Albrektienė et al. 2012). In this research work, UV-254 absorbance was measured using a spectrophotometer type Perkin Elmer with a quartz cell of 1 cm path length.

The potential of hydrogen (pH) is an important parameter which allows an aqueous solution to be defined acidic or basic. This research studied the effect of the pH change on the effectiveness of the CF treatment, where a Metrohm 744 pH-Meter instrument was used.

Coagulation/flocculation experiments

In order to develop a sustainable management model for the removal of dissolved organic matter from Timgad dam water, several CF experiments were conducted. CF experiments were performed according to the jar test standard procedure (ASTM International 2008) using the jar test apparatus type Bio block, Scientific, flocculator 10405 equipped with four beakers. Each beaker contained 150 mL of water to be treated. The treatment was conducted in three steps in accordance with the operating conditions previously optimized in the laboratory. The following section shows the experiments that were conducted in order to assess the treatment efficiency of the CF process, and different coagulants and flocculants (coagulant aids) were used to determine the suitable chemical nature and dosing rate. In fact, five coagulants were tested in this study: aluminum sulphate $Al_2(SO_4)_3$, iron (III) chloride $FeCl_3$, magnesium chloride $MgCl_2$, ammonium sulphate $(NH_4)_2$-SO_4 and calcium chloride $CaCl_2$ at usual doses between 0 and 200 mg/L, while one flocculant CHT-Flocculant CV (also called guanidine, a cyano-polymer with ammonia and formaldehyde, which is a cationic polymer of low molecular weight) was tested using a concentration ranging from 0 to 100 mg/L. All CF experiments were performed in accordance with the operating conditions previously optimized in the laboratory (results not shown), which were in conformity with those adopted by Malkoske et al. (2020) in the treatment of drinking water: (i) the coagulant was added to water under rapid mixing at 150 rpm for 3 min; (ii) after coagulation, the pH of water samples was adjusted to neutrality and flocculant was added under slow mixing at 30 rpm for 15 min; (iii) then, samples were allowed to settle down for decantation for 30 min. Prior to coagulant addition, the pH of water samples was adjusted to the desired value, in the range of 5 to 9, by the addition of H_2SO_4 or NaOH solution (0.1 M) whereas after the coagulation step and before adding the CHT flocculant CV, the pH of the coagulation sampled was adjusted up to neutrality (Louhıchı et al. 2019).

Optimization of CF process using RSM approach

The conventional 'one-factor-at-a-time-method' approach is laborious and time-consuming, especially for a large number of variables. Moreover, it seldom guarantees the determination of optimal conditions (Choudhari & Singhal 2008). These limitations of a single factor optimization process can be overcome by using statistical methods. For this purpose, response surface methodology (RSM) was used as optimization method. RSM, also known as Box–Wilson methodology, is an optimization method applying statistical techniques based upon the factorial designs of central composite design (CCD) and Box–Behnken design (BBD). An RSM approach will not only be able to determine the optimum conditions from a minimal number of experiments, but also give the information to estimate results in order to design a process (Humbird & Fei 2016).

In order to optimize the removal of the DOM from the Timgad dam water, a CCD model based on three factors was

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used as the experimental design model (Table 1). Coagulant concentration (50–150 mg/L), flocculant concentration (10–70 mg/L), 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 Timgad dam water. Coagulant (X_1), flocculant dose (X_2), and pH (X_3) 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 equation (Equation (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 a 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 and X_j, α_{ij} is the quadratic effect of input factor X_i, and ε is the error.

Responses included in this model are the removal efficiency (R%) in terms of COD and in terms of UV-254 nm of the treated samples.

Removal efficiencies were calculated according to Equation (2):

$$\text{Removal efficiency } (R\%) = \left(\frac{C_0 - C_{ec}}{C_0}\right) \times 100 \quad (2)$$

where C_0 is the initial concentration, and C_{ec} is the concentration in the treated simple.

The statistical analysis of CCD experimental results, response surface modeling, graph plotting and optimization of process variables were carried out using the statistical NemrodW software (version 2000-D). The validity of the statistical model was performed by comparing the experimental values with predicted ones.

Table 1 | Experimental range and levels of independent factors

Coded factors	Factors	Coded levels		
		−1	0	+1
X1	Coagulant concentration (mg/L)	50	100	150
X2	Flocculant concentration (mg/L)	10	40	70
X3	pH	5	7	9

Table 2 | Experimental results of CCD-designed experiments for CF treatment of Timgad dam water

Run no.	Factors			Responses		
	X1 (mg/L)	X2 (mg/L)	X3 (–)	Y1 (%)	Y2 (%)	Y3
1	50	10	7	20.33	24.63	6.9
2	50	10	7	20.39	24.63	6.9
3	150	10	7	50.45	47.82	6.84
4	150	10	7	50.51	49.27	6.83
5	50	70	7	21.48	26.08	7.05
6	50	70	7	21.72	26.08	7.02
7	150	70	7	56.84	57.97	6.91
8	150	70	7	56.84	57.97	6.92
9	50	40	5	14.90	39.12	6.98
10	50	40	5	14.84	37.68	6.96
11	150	40	5	48.21	52.17	6.92
12	150	40	5	48.28	52.17	6.94
13	50	40	9	8.14	15.94	6.90
14	50	40	9	8.26	15.94	6.92
15	150	40	9	9.95	20.28	6.83
16	150	40	9	10.01	20.28	6.76
17	100	10	5	46.16	42.02	6.73
18	100	10	5	46.28	42.02	6.70
19	100	70	5	47.97	44.92	6.73
20	100	70	5	48.03	44.92	6.74
21	100	10	9	9.29	18.84	6.74
22	100	10	9	9.35	18.84	6.75
23	100	70	9	10.01	21.73	6.77
24	100	70	9	10.07	23.18	6.81
25	100	40	7	56.72	59.42	6.74
26	100	40	7	56.66	59.42	6.69
27	100	40	7	56.72	59.42	6.76
28	100	40	7	56.72	59.42	6.75
29	100	40	7	56.72	59.42	6.76

RESULTS AND DISCUSSION

Water characterization

The present investigation follows on from previous studies focused on the characterization of Timgad's dam water (Tiri *et al.* 2017; Khettaf & Bouhelassa 2018; Amrane & Bouhidel 2019). The mentioned studies provided an

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overview of the water quality of Timgad's dam water and the temporal variations of different water quality indicators. The main result found by these authors is that the water samples were charged with DOM (average concentration around 14 mgO_2/L) with a small variation as a function of environmental factors (COD ranged from 10 to 16 mgO_2/L). Therefore, in order to study the physicochemical characteristics of real untreated Timgad dam water and to carry out the coagulation/flocculation treatment, a water sample was collected from the Timgad dam according to *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). The physicochemical characterization obtained is summarized in Table 3.

The analysis of the water sample collected from the Timgad dam (Table 3) showed that the dam water is charged with dissolved organic matter. Prior treatment should be considered to improve the quality of Timgad's dam water in order to satisfy the expectations of public authorities (Décret exécutif n° 11-125 du 17 Rabie Ethani 1432) and most importantly to protect human health.

Screening of chemical reagents/flocculant

The results obtained during the first step are presented in the following section.

Effect of the nature and concentration of the coagulant

Adding coagulant chemicals having an opposite charge to those of pollutants present in the water contributes to the charge neutralization of non-settlable solids such as organic matter. Once neutralization of the charge is accrued, the small suspended particles are capable of sticking together and forming microflocs not visible to the naked eye. The rapid mixing is needed to disperse the coagulant effectively and promote particle collisions.

Colloidal dissolved organic matter in water has an electrical charge, which is generally negative. Since they all have the same charge, they repel each other and do not tend to form larger aggregates, and are therefore easier to remove. The addition of coagulants makes it possible to destabilize the colloidal materials, and thus to allow them to agglomerate in order to easily eliminate them by decantation or by filtration. Among the five tested coagulants (Figures 2 and 3), aluminum sulphate $Al_2(SO_4)_3$ and iron (III) chloride $FeCl_3$ show significant rates of reduction. In fact, the highest removal rate is observed for the $Al_2(SO_4)_3$. Indeed, the efficiency of DOM removal increases with the increase in the dose of coagulant, where the efficiency reaches a maximum reduction rate of 59% in terms of COD and 63% in terms of UV-254 at a dose of 100 mg/L coagulant. Previous work reported similar results (Guida *et al.* 2007; Di Bella *et al.* 2014).

It is important to mention that, at an initial pH (pH of raw water) equal to 6.56 (pH above 5), the higher the coagulant dosage used, the higher the dissolved organic matter removal obtained. In fact, in the case of aluminum sulfate, a higher dosage above 100 mg/L was required to enhance

Table 3 | Physico-chemical characterization of the studied sample water

Parameter	Value	Algerian norm for potable water
COD (mgO_2/L)	16.57	/
pH	6.56	≥6.5 and ≤9
Conductivity (μs/cm)	868	2,800
Cl^- (mg/L)	110	500
NO_3^- (mg/L)	0.60	50
K^+ (mg/L)	3.12	12
Na^+ (mg/L)	30.65	200
SO_4^{2-} (mg/L)	432	400

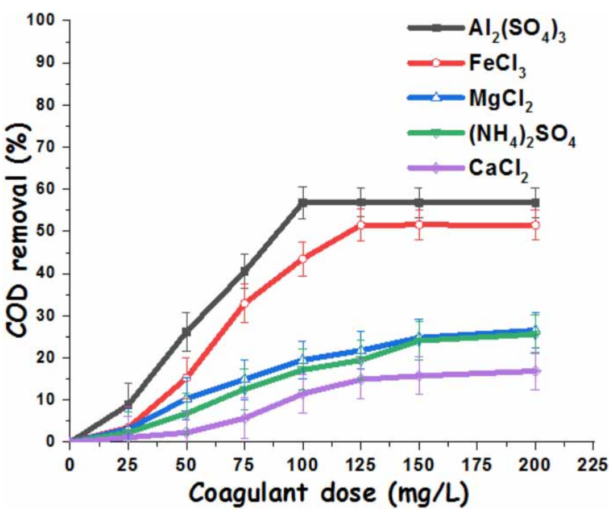

Figure 2 | Effect of coagulant nature and concentration on the COD removal at pH = 6.56 and 50 mg/L of CHT flocculant CV.

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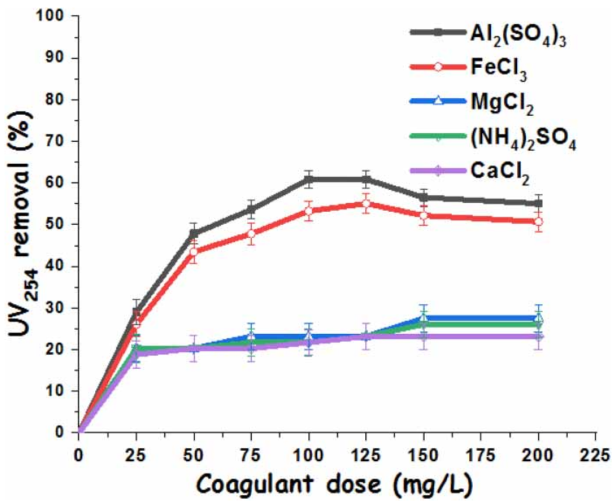

Figure 3 | Effect of coagulant nature and concentration on the UV-254 removal at pH = 6.56 and 50 mg/L of CHT flocculant CV.

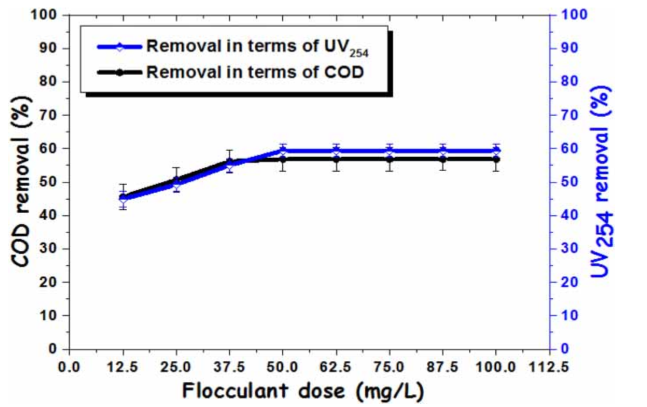

Figure 4 | Effect of flocculant concentration on COD and UV-254 removals at pH = 6.56 and 100 mg/L of aluminum sulfate.

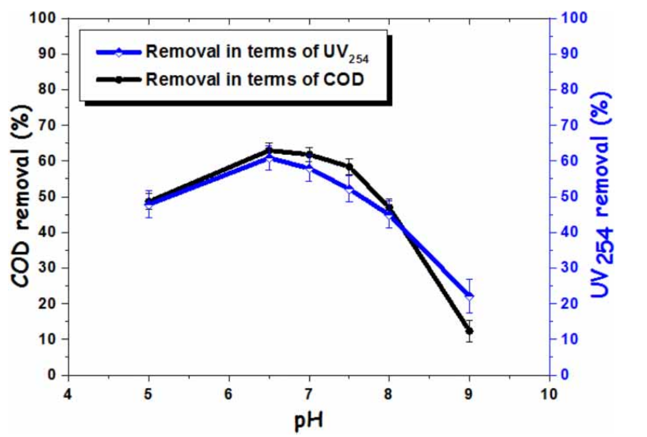

Figure 5 | Effect of initial pH on COD and UV-254 removal under 100 mg/L of aluminum sulfate and 50 mg/L of CHT flocculant CV.

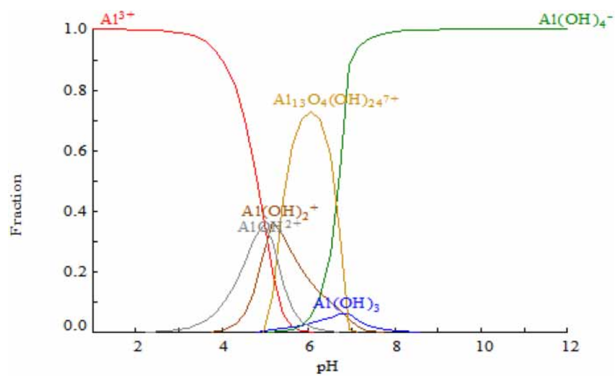

Figure 6 | Species distribution of aluminum as function of pH using the Hydra–Medusa software.

the DOM removal. In this condition, it is very likely that the removal mechanism of DOM is predominantly by sweep flocculation. Sweep flocculation requires a high dose of coagulant to promote aluminum hydroxide ($Al(OH)_3$) formation in the pH range 5.5–7.5 (Gone *et al.* 2008). This process has become known as 'sweep flocculation' since particles are 'swept out' from the water by an amorphous hydroxide precipitate. Another explanation was referred to when describing the removal of DOM in terms of COD during CF by Jiang (2015); they suggested that the use of the coagulant combined the small suspended particles in the water to be treated into small aggregates (flocs). Then these small flocs formed were also combined with each other with the aid of a flocculant to form large settleable aggregates (blocks). These formed blocks have the capacity to adsorb the dissolved organic matter, which allows its removing by a simple solid/liquid separation process.

Effect of flocculant concentration

Adding coagulant-aid (flocculant) increases the particle size from submicroscopic microfloc to visible flocs. In fact, during a longer contact time at the gentle mixing stage, floc size continues to build with additional collisions and interaction with added polymers. The larger the flocs that formed, the higher the settling rate.

The results obtained (Figure 4) showed that the addition of the flocculant at low concentrations, between 12.5 and

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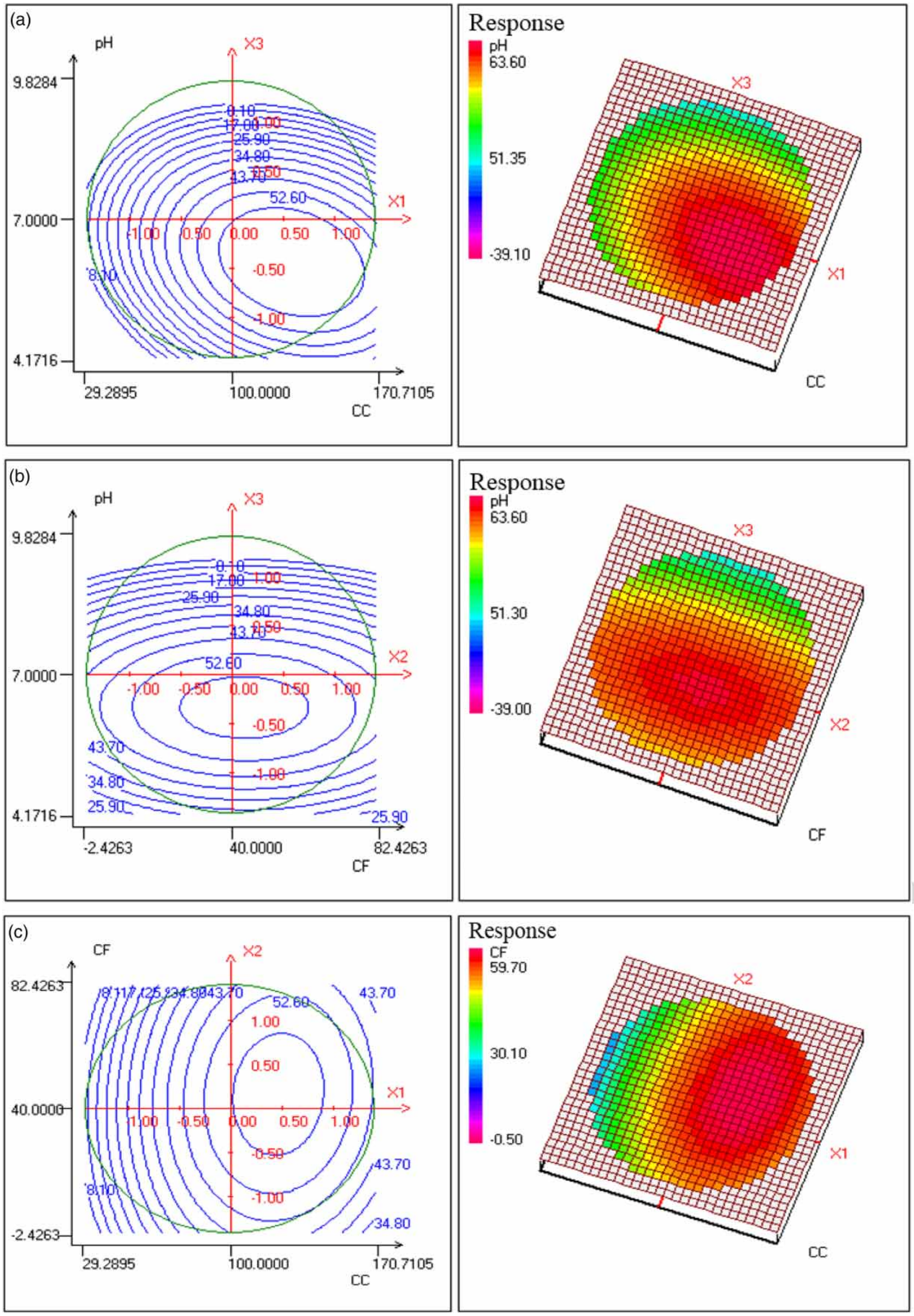

Figure 7 | Two-dimensional and three-dimensional response surface plots for the COD removal from Timgad's dam water using CF treatment as a function of: (a) coagulant concentration and pH (flocculant concentration = 50 mg/L), (b) flocculant concentration and pH (coagulant concentration = 100 mg/L) and (c) coagulant concentration and flocculant concentration (pH = 7).

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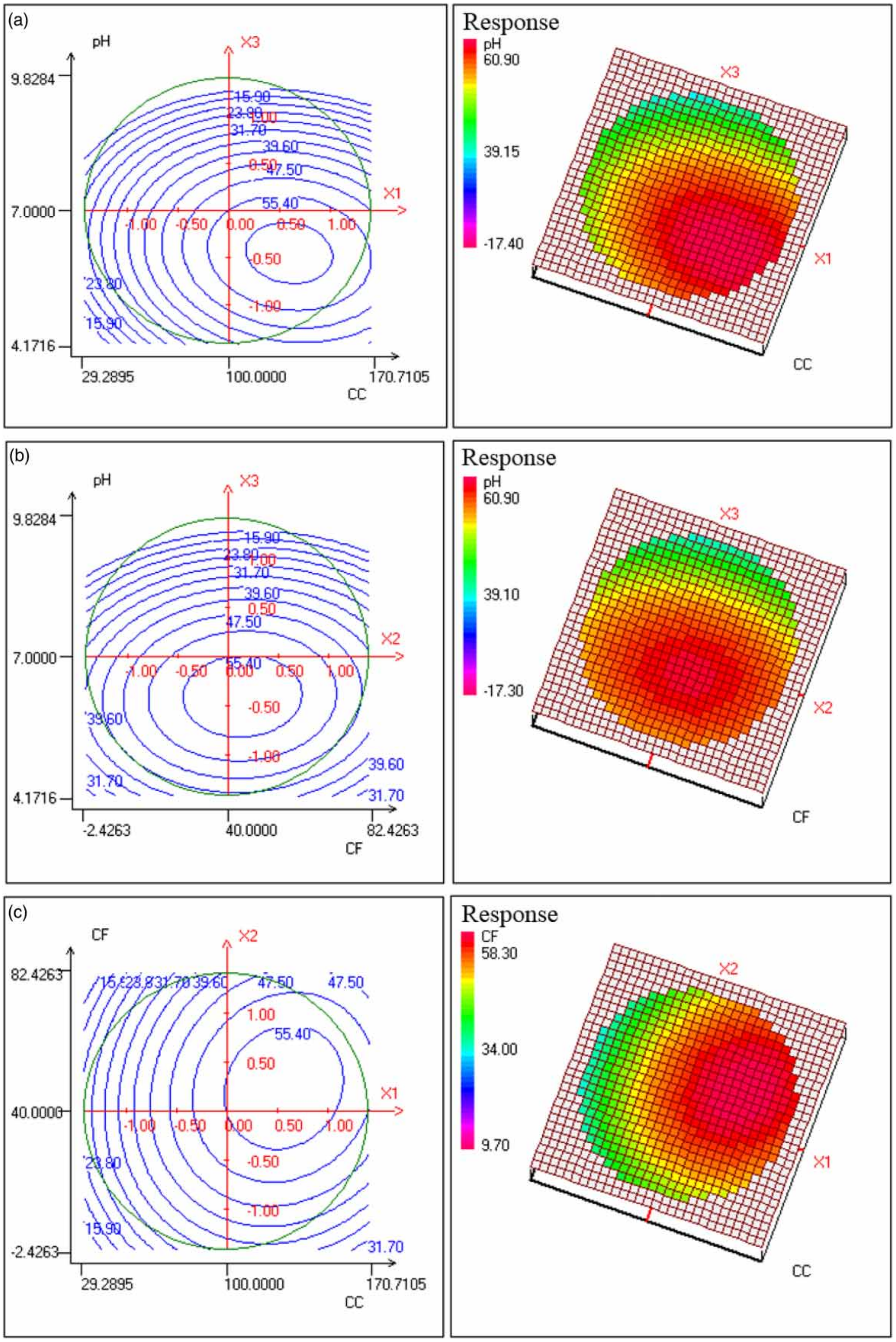

Figure 8 | Two-dimensional and three-dimensional response surface plots for the UV-254 removal from Timgad's dam water using CF treatment as a function of: (a) coagulant concentration and pH (flocculant concentration = 50 mg/L), (b) flocculant concentration and pH (coagulant concentration = 100 mg/L) and (c) coagulant concentration and flocculant concentration (pH = 7).

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100 mg/L with $Al_2(SO_4)_3$ as coagulant, improves the efficiency of the elimination of dissolved organic matter. However, a significant improvement is observed from a concentration of flocculant of 50 mg/L. Beyond this concentration, the elimination yield remains stable, so this concentration of 50 mg/L is retained for the rest of the study.

Effect of the initial pH

The obtained results in Figure 5 show that the optimal pH for the highest elimination rates were obtained at pH in range of 5 to 7. This can be explained as follows: in acidic conditions, numerous monomeric and many possible positively charged polynuclear forms of aluminum sulfate hydrolysis products can be formed including Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$. These compounds are responsible for the removal of charged dissolved organic matter by binding to anionic sites, thus neutralizing their charge and giving a reduced solubility. Figure 6 illustrates the species distribution of aluminum as a function of pH. For pH superior to 7 (alkaline conditions), the elimination efficiency decreased. This trend could be attributed to the formation of aluminum hydro-complexes (Pinotti & Zaritzky 2001).

Optimization of CF process using RSM approach

RSM is a very useful tool that can be used to optimize many types of experimental processes. In this technique, the controlled factors are called input variables and the output results are called response variables. In order to screen the appropriate parameters and determine the experimental domain, several preliminary experiments were carried out. The results obtained from the jar test experiments showed that the use of aluminum sulphate as a coagulant at a concentration equal to 100 mg/L, with a flocculant dose equal to 50 mg/L at an initial pH value near to 7, appears to be the most suitable choice which gives the highest DOM removal efficiency and the lowest consumption of coagulant and flocculant. The effects of coagulant concentration (X_1), flocculant concentration (X_2), and initial solution pH (X_3) were monitored on three responses: COD removal (Y_1), UV-254 removal (Y_2), and final pH (Y_3). Table 2 shows the coded experiments conducted according to experimental design along with the response values.

The analysis of CCD experimental results, response surface modeling (Figures 7 and 8), and optimization of process variables were carried out using NemrodW software. The statistical analysis employed Fisher's *F*-test and Student's *t*-test and are registered in Table 4. In general, the larger the magnitude of *t* and the smaller the value of *p*, the more significant is the corresponding coefficient term (Tripathi *et al.* 2009). 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

Table 4 | Estimated regression coefficient for CF treatment of Timgad's dam water

	Coefficient value			*F* inflation			Standard deviation			*t* exp			*p*-value		
RC	Y1	Y2	Y3	Y1	Y2	Y3	Y1	Y2	Y3	Y1	Y2	Y3	Y1	Y2	Y3
$\alpha 0$	56.708	55.420	6.740				0.028	1.369	0.010	2,041	40.49	659.72	***	***	***
$\alpha 1$	12.564	9.239	−0.042	1.00	1.00	1.00	0.016	0.765	0.006	808.79	12.08	−7.44	***	***	***
$\alpha 2$	1.263	2.551	0.035	1.00	1.00	1.00	0.016	0.765	0.006	81.31	3.33	6.13	***	**	***
$\alpha 3$	−14.975	−12.126	−0.014	1.00	1.00	1.00	0.016	0.765	0.006	−963.97	−15.85	−2.41	***	***	*
$\alpha 11$	−13.729	−8.611	0.168	1.03	1.03	1.03	0.024	1.160	0.009	−582.73	−7.42	19.41	***	***	***
$\alpha 22$	−5.659	−7.503	0.013	1.03	1.03	1.03	0.024	1.160	0.009	−240.20	−6.47	1.52	***	***	
$\alpha 33$	−22.655	−15.112	−0.007	1.03	1.03	1.03	0.024	1.160	0.009	−961.61	−13.02	−0.79	***	***	
$\alpha 12$	1.280	1.994	−0.014	1.00	1.00	1.00	0.022	1.082	0.008	58.26	1.84	−1.70	***		
$\alpha 13$	−7.899	−2.357	−0.019	1.00	1.00	1.00	0.022	1.082	0.008	−359.53	−2.18	−2.32	***	*	***
$\alpha 23$	−0.264	0.933	0.006	1.00	1.00	1.00	0.022	1.082	0.008	−12.01	0.86	0.77	***		

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insignificant terms for COD removal ($Y1$), UV-254 removal ($Y2$), and final pH ($Y3$) of the treated water were obtained from Equations (3)–(5) respectively:

$$\boldsymbol{Y1} = 56.708 + 12.564X1 + 1.263X2 - 14.975X3 - 13.729X1^2 - 5.659X2^2 - 22.655X3^2 + 1.280X1X2 - 7.899X1X3 - 0.264X2X3 \quad (3)$$

$$\boldsymbol{Y2} = 55.420 + 9.239X1 - 12.126X3 - 8.611X1^2 - 7.503\,X2^2 - 15.112X3^2 \quad (4)$$

$$\boldsymbol{Y3} = 6.740 - 0.042X1 + 0.035X2 + 0.168X1^2 \quad (5)$$

A positive sign indicates a synergistic effect, whereas a negative sign indicates an antagonistic effect. Analysis of variance (ANOVA) is always required to determine the significance and adequacy of mathematical models proposed by RSM and for this reason, 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 the quadratic effect, respectively. For all models, analysis of variance (ANOVA) for COD removal ($Y1$), UV-254 removal ($Y2$) and final pH ($Y3$) showed that fitted second-order response surface models were highly significant (Table 5). The R^2 value of 0.960 for Equation (2), of 0.917 for Equation (3), and of 0.885 for Equation (4) were considered relatively high except for Equation (4), indicating that there was a good agreement between the experimental and the predicted values taken from the models. The regression coefficients and the interaction between each independent factor could be considered statistically significant for p-values below 0.01 with a 99% confidence interval. These results indicated that the accuracy of the polynominal models was well adapted. Compared with other studies adopting RSM and Box–Behnken design statistical analysis for the optimization of industrial wastewater treatment (Khouni *et al.* 2011; Louhıchı *et al.* 2019), our obtained models were considered highly significant and indicated excellent correlations between the experimental results and the predicted values of COD and UV-254 removal taken from these models.

Table 5 | Analysis of variance (ANOVA) for the fitted quadratic polynomial models of CF treatment of Timgad's dam water (effect of coagulant concentration, flocculant concentration and pH)

RC		**Sum of squares (SS)**			**Mean square (MS)**			**Ratio/$F_{statistics}$**			***p***		
Sources of variation	**Degree of freedom (DF)**	**Y1**	**Y2**	**Y3**	**Y1**	**Y2**	**Y3**	**Y1**	**Y2**	**Y3**	**Y1**	**Y2**	**Y3**
Regression	9	1.10594×10^4	5.96944×10^3	0.2589	1.22883×10^3	6.63271×10^2	0.0288	318,245.5349	70.8246	55.1181	<0.01 ***	<0.01 ***	<0.01 ***
Residual	19	4.58588×10^2	5.39684×10^2	0.0338	2.41362×10	2.84044×10	0.0018						
Total	28	1.15180×10^4	6.50913×10^3	0.2927									

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CONCLUSION

This research work aimed to optimize the coagulation/flocculation process for maximum DOM removal from Timgad's dam waters. For this purpose, preliminary jar test experiments were conducted under different treatment conditions. Once the appropriate nature and dosage of coagulant ($Al_2(SO_4)_3$ of about 100 mg/L), dosage of flocculant (CHT-flocculant CV of about 50 mg/L) and initial pH (pH = 7) were identified, optimization using RSM via Box–Behnken design was applied in order to enhance the treatment efficiency. The effects of three influencing factors (coagulant concentration, flocculant concentration and initial pH) and their interactions on the efficiency of the DOM elimination were also studied. The results obtained from the regression models showed that the maximum DOM removal was achieved under the following optimal conditions: 133 mg/L of $Al_2(SO_4)_3$, 60 mg/L of CHT-flocculant CV and initial pH equal to 6.91. Under these conditions, the final pH of the treated effluent was about 6.78 while UV-254 and COD removal rates reached 56% and 59%, respectively.

Overall, these findings on treated Timgad dam water quality and coagulation/flocculation treatment demonstrated that the optimizing method using RSM is a very effective technique, as it allows the saving of time, reduces chemical usage and allows the highest treatment efficiency to be reached. The obtained results can be useful for application in Timgad's treatment plant in order to provide a 'super treated water' with the lowest organic matter content.

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DISCLOSURE STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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