Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27229

225 (2021) 175–189
June

Modeling and optimizing of coagulation–flocculation process by response surface methodology for rehabilitation of tannery wastewater treatment plant

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Received 23 October 2020; Accepted 4 March 2021

ABSTRACT

This work aims to optimize coagulation–flocculation operational parameters using chitosan as a biocoagulant to reach a satisfying reduction rate of chemical oxygen demand (COD), chloride concentration and suspended materials in an alkaline pH. This process is suggested as pretreatment before the biological step and a comparison study with aluminium sulphate is conducted. In the first part, nine factors were screened by Plackett–Burman experimental design to identify the most significant, that is, for coagulant: weight percentage of chitosan mixed to aluminium sulphate, dosage, mixing rate and stirring time, for flocculent: dosage, stirring time, mixing rate also initial pH and settling time. In the second part, modelling and optimization of the chosen responses were established by Doehlert design. The target responses, that is, pH: 8.6, COD: 592 mg O_2/L, suspended matter (SM): 12.8 mg/L and [Cl]: 2,889 mg/L were obtained with the following optimal conditions: dosage of chitosan = 612.8 mg/L, a stirring speed of 6 rpm at an initial pH of 8.8, and 5.6 mg/L of flocculant with a stirring speed of 43 rpm followed by a settling time of 22 min. The most significant abatements obtained for COD, SM and [Cl] are 68.90%, 95.24% and 39.72%, respectively. Chitosan was found to be an efficient eco-friendly coagulant, forming less sludge than aluminium sulphate and allowing the industry to reduce treatment costs.

Keywords: Coagulation–flocculation; Experimental design; Optimization; Tannery wastewater

1. Introduction

Treating industrial wastewater is of concern for authorities and policymakers for preserving a healthy environment and human beings. The leather tanning industry is widely recognized as among the most polluting industries through its huge consumption and wasting of water [1]. It is a wide common industry all over the world and is known to be one of the most important industries in Mediterranean Countries [2,3]. For instance, a small tannery located in Tunisia, with a treatment of 1,200 skins/d induces up to 80 m^3 of effluents according to Boujelben et al. [4]. It can entail harmful contamination of water with a high level of salinity, inorganic matter, biochemical/chemical oxygen demands, suspended solids, ammonia, organic nitrogen and specific pollutants [5]. Too much effort has been done so far to develop cost-effective wastewater treatment technologies to reduce discharge effluent pollutants and reach discharge standards. The need for developing these technologies for treating tannery effluent while reducing sludge production rate and chemical consumption is still apparent [6–8]. Conventionally the tannery effluent is treated by two principal processes that consist of primary treatment to remove suspended solids followed by a second biological

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treatment process to remove colloidal organic matter, chemical oxygen demand (COD) and dyes. Coagulation–flocculation (CF) used in primary treatment, has been reported as a typical chemical treatment technique that enhances the ability of a treatment process to remove suspended solids, turbidity and reduce the pollution load, improving the removal efficiency of the treatment process [9,10]. CF has been widely used as a chemical process in industrial and urban wastewater treatment to achieve the solid–liquid separation since it can be easily implemented and operated with low-cost energy consumption [11,12]. In general, CF performed using chemical inorganic salts such as aluminium and ferric sulphate and chloride. Jar tests are usually conducted in two stages mixing process which involves rapid stirring and slow stirring performed by using in the first step a coagulant such as iron(III), aluminium salts [13,14] and after in the second step a flocculant [15,16]. Various polyelectrolytes with a different structures such as polysaccharides and polyaluminum chloride, among others, are commonly used as coagulants to enhance the sedimentation rate. Besides some unconventional adsorbents like tea waste and black gram husk have been studied to remove heavy metal from industrial effluents [17,18]. Recent studies [19–22] showed that natural coagulants can be as performant as chemical coagulants in the sedimentation process and their applications in industrial wastewater treatment are gaining popularity. Natural coagulants can be derived from crops such as maize, *Moringa oleifera* and okra mucilage. It can also have an animal origin such as chitosan which is a co-polymer produced by the deacetylation of chitin [23]. It can be extracted from crushing shells of lobsters, crabs and shrimps [24]. It has many properties such as non-toxicity, biodegradability and outstanding chelation behaviour making it an effective coagulant or flocculent used to remove contaminants in the dissolved state like dye and suspended solids [25]. Renault et al. [26] reported that chitosan has the advantages of being non-toxic material, non-corrosive and safe to handle. In addition, chitosan is efficient in cold and ambient water temperature and does not leave residual metals that can cause secondary contamination problems [27]. The study of Verma et al. [25] revealed that chitosan considerably increases the density of sludge and facilitates its drying compared to the sludge produced with metal salts. In addition, as biopolymers are biodegradable, the sludge can be efficiently degraded by micro-organisms. Previous studies showed that salts influence the COD removal rate by inhibiting the activity of natural habitat microbes presented in raw tannery wastewater, thus, affecting the good aerobic biological treatment [28,29]. In addition, chitosan does not add much to the salinity of the treated water and is used in alkaline pH. Therefore, this biopolymer is used in this study and its performance efficiency was compared with aluminium sulphate.

The aim of this paper is to optimize the use of the coagulant and operational conditions to reach a satisfying reduction rate of COD, chloride concentration and suspended materials in an alkaline pH with the coagulation–flocculation process. The effluent produced upstream within this unitary operation, will feed directly to a biological reactor. Studying many parameters at one time is very difficult. For this reason, the design of experiments (DoE) is used in order to model and optimize the chosen responses. DoE is considered necessary to provide robust and accurate solutions to CF problems [30]. In the first step, Plackett–Burman matrix is applied in view to determine the most significant factors and investigate the interactive effects of experimental factors. After that, in the second-step, the Doehlert matrix enables us to model and optimize our responses in order to obtain the biodegradable effluents, which will be treated biologically later. This statistical methodology improves the reliability and relevance of the experiments since it allows to study of many factors simultaneously with minimum experiments and high precision information. The optimization of the operational conditions is significantly helpful to improve CF operations and reduce both chemical consumption and operating costs [31].

2. Material and methods

2.1. Wastewater characteristics

The effluent was sampled from a homogenization tank in which the streams of each drained bath of the tanning process are collected together. It is located just upstream of the CF treatment of the wastewater treatment plant where tannery effluent is pre-treated before the biological treatment. Samples were then taken into the laboratory for experimental runs. The main physical–chemical characteristics of the tannery wastewater are illustrated in Tables 1 and 2 and cations amounts were determined by inductively coupled plasma–atomic emission spectrometer (Analytik Jena Quant PQ 9000 Elite, Germany). The sludge samples of untreated and treated effluent were dried after settling and their morphology was characterized by a FEI Quanta 200 high-resolution scanning electron microscope (SEM).

2.2. Materials

The aluminium sulphate hexadecahydrate ($Al_2(SO_4)_3\cdot 16H_2O$) was used as a coagulant while Zetag was used as a flocculant. These reagents were provided by Fisher Scientific U.K. Ltd., (United Kingdom) and O-BASF Company, (United States) respectively. The chitosan which is a biocoagulant was delivered from Sigma-Aldrich (United States) (shrimp shells ≥ 75% deacetylated) and used to substitute the aforementioned chemical coagulants. All these reagents were used as a powder in order to avoid the dissolution step.

2.3. Experimental procedure

The CF experiments were performed using 500 mL of wastewater sample in each beaker in a conventional jar test apparatus model JLT 4 Floc tester QA1014X. The aqueous solution was then rapidly mixed at a paddle speed of 300–600 rpm for 2–7 min to ensure a homogeneous and even distribution of the chemicals in the wastewater. Then, the solution is mixed at a slow rate (10–60 rpm) for 2–10 min to allow the flocculation process. During the latter phase, the coagulant was introduced in variable doses to assess its performances. After allowing the settling to occur for 10–30 min, a volume of 25 mL of the liquid was

Table 1
Physical–chemical characteristics of tannery effluents

Parameter	pH	COD	SM[a]	λ[b]	[Cl][c]	Turbidity	Ca	K	Mg	Na
Value	9.1	1,902 mgO_2/L	269 mg/L	11,670 µS/cm	4,792.5 mg/L	1,200 NTU	9.72 mg/L	5.17 mg/L	637.88 mg/L	637.88 mg/L
Parameter	Mo	Ni	Pb	Zn	Cr	Cd	Fe	Mn	Cu	As
Value	<DL	0.001 mg/L	<DL	0.048 mg/L	<DL	0.003 mg/L	0.049 mg/L	<DL	<DL	<DL

[a]suspended matter; [b]conductivity; [c]chloride concentration.

Table 2
Main physical–chemical characteristics of tannery effluents used as responses

Response	pH	COD	SM	λ	[Cl]
Unit	–	mg O_2/L	mg/L	µS/cm	mg/L
Value	9.1 ± 0.2	1,902 ± 4	269 ± 3	11,670 ± 10	4,792.5 ± 5
Symbol	Y_1	Y_2	Y_3	Y_4	Y_5

sampled using a pipette from a height of about 3 cm below the liquid surface in each jar.

2.4. Experimental design

The coagulation was conducted with varying the percentage of chitosan weight mixed to aluminium sulphate to investigate its efficiency in comparison with the last one. Only the Zetag was used for flocculation. Zetag is an acrylamide and acrylic acid copolymer prior to mechanical or static solid–liquid separation. It is highly effective across a wide range of wastewater treatment applications.

Nine factors (X_i) were considered to set-up the experimental design. The independent variables of these factors as well as their levels in actual and coded values, symbols and units are listed in Table 3.

These factors were selected according to the steps towards jar test experiments and are represented by +1 for high level, 0 for centered level and –1 for low level.

3. Results and discussion

3.1. Factors screening

3.1.1. Plackett–Burman matrix

Table 4 reports the Plackett–Burman matrix built by screening the 3 levels for the 9 factors (from X_1 to X_9) and 5 responses (from Y_1 to Y_5) for the CF process. This matrix involves 12 experiments realised in a random assignment and five repeated centered points, corresponding to level 0. The five responses selected are: pH, COD, suspended matter (SM), conductivity (λ) and chloride concentration ([Cl]).

3.1.2. Sensitivity analysis of the experimental factors

Table 5 shows the coefficient and significance of the regressions between the experimental factors and response variables studied using Plackett–Burman matrix. The Plackett–Burman design (PBD) is an efficient screening method to identify the important factors among a large number of factors that influence a process [32,33]. PBD was used to select the significant factors out of 9 factors considered in this study that influence the efficiency of the wastewater treatment process. For mathematical modelling the following first-order polynomial model was used:

$$Y_i = \beta_0 + \sum_i \beta_i X_i \quad (1)$$

where Y is the predicted response, β_0 is the model intercept and β_i is the linear coefficient and X_i is the level of the independent variable.

Eq. (1) was applied for the 5 responses studied:

- For pH, $Y_1 = a_0 + \sum_i a_i X_i$
- For COD, $Y_2 = b_0 + \sum_i b_i X_i$
- For SM, $Y_3 = c_0 + \sum_i c_i X_i$
- For λ, $Y_4 = d_0 + \sum_i d_i X_i$
- For [Cl], $Y_5 = e_0 + \sum_i e_i X_i$

The more significant experimental parameters are indicated in Table 4 by stars [[a]for high significance (P < 0.01%), [b]for medium significance (P < 0.1%) and [c]for low significance (P < 5%)]. The results show that coagulant dosage (X_2), stirring time (X_4), initial pH (X_5), flocculant dosage (X_6), mixing rate of flocculent (X_7) and settling time (X_9) are the most significant and influencing factors on the CF process responses. As stated by Wei et al. [34], inadequate doses of coagulants or flocculants (X_2, X_6) evolve over a weak charge neutralization and bridging effects. Meanwhile, excessive doses might cause sludge particles to be covered with coagulants/flocculants, resulting in the regeneration of the suspension stability of flocs. pH has

Table 3
Actual and coded values of independent variables used for experimental design

Factors names	Unit	Symbol	Levels and coded values		
			–1	0	1
Weight percentage of chitosan mixed to $Al_2(SO_4)_3{\cdot}16H_2O$	%	X_1	0	50	100
Coagulant dosage	mg/L	X_2	300	500	700
Mixing rate of coagulant	rpm	X_3	300	450	600
Stirring time of coagulant	min	X_4	2	4.5	7
Initial pH	–	X_5	8	9	10
Zetag flocculent dosage	mg/L	X_6	2	4.5	7
Mixing rate of flocculent	rpm	X_7	10	35	60
Stirring time of flocculent	min	X_8	2	6	10
Settling time	min	X_9	10	20	30

Table 4
Plackett–Burman matrix design and observed values of the chosen responses

N°. Exp.	Studied factors									Observed responses				
	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	pH (Y_1)	COD (Y_2)	SM (Y_3)	λ (Y_4)	[Cl] (Y_5)
1	1	–1	1	–1	–1	–1	1	1	1	8.5	732	18.0	11,870	4,828
2	1	1	–1	1	–1	–1	–1	1	1	9.0	900	13.0	11,500	4,792.5
3	–1	1	1	–1	1	–1	–1	–1	1	8.3	900	24.0	12,050	4,437.5
4	1	–1	1	1	–1	1	–1	–1	–1	8.4	585	22.0	11,930	5,147.5
5	1	1	–1	1	1	–1	1	–1	–1	8.0	600	20.0	11,950	4,934.5
6	1	1	1	–1	1	1	–1	1	–1	8.0	900	18.0	11,950	4,615
7	–1	1	1	1	–1	1	1	–1	1	9.3	300	20.0	11,640	4,615
8	–1	–1	1	1	1	–1	1	1	–1	8.3	585	21.0	11,950	4,792.5
9	–1	–1	–1	1	1	1	–1	1	1	9.1	300	23.0	11,880	5,254
10	1	–1	–1	–1	1	1	1	–1	1	8.2	439	20.0	11,660	5,325
11	–1	1	–1	–1	–1	1	1	1	–1	8.6	1,500	27.0	11,910	4,970
12	–1	–1	–1	–1	–1	–1	–1	–1	–1	8.2	900	19.5	11,980	4,260
13	0	0	0	0	0	0	0	0	0	9.0	900	17.0	11,370	4,615
14	0	0	0	0	0	0	0	0	0	8.3	732	22.5	12,030	5,041
15	0	0	0	0	0	0	0	0	0	9.4	900	17.5	11,530	5,183
16	0	0	0	0	0	0	0	0	0	8.4	750	20.0	11,980	4,899
17	0	0	0	0	0	0	0	0	0	9.5	600	15.5	11,170	4,970

also an important effect on the efficiency of the removal of pollution since surface charges of colloidal particles in wastewater and coagulants/flocculants vary under different pH levels. As reported by BinAhmed et al. [35], mixing time had an effect on the floc's resistance. Pollutant removal efficiency is not only dependant on mixing speed also on mixing time, such that a higher fast mixing speed is required for shorter mixing time.

The regression coefficients (Table 7) confirm the effect of each parameter on the followed responses. Recently, it was reported that there is a correlation between all the parameters and the improvement of water quality. Besides the variation of one parameter affects the other one. Thus, it was important to determine the most influencing parameters and to model the interaction between them and their effect on the response [36,37].

The weight percentage of chitosan mixed with aluminium sulphate (X_1) has no effect on the pH, SM and conductivity responses. However, its effect on the COD and [Cl] responses is slightly significant (*P*-value equal to 2.17% and 3.70%, respectively). However, chitosan shows good abatement values of COD (68%), SM (95%) and Cl concentration (40%) as compared to aluminium sulphate which gives either same or a little bit better abatement for COD but it increases salts amount in the effluent as confirmed also by Lofrano et al. [38]. Chitosan seems to be in competition with aluminium sulphate. In addition, Fig. 1 shows that the amount of sludge formed using 100% chitosan (Fig. 1b) is much smaller than that formed using aluminium sulphate alone (Fig. 1c).

In fact, SEM was used to characterize chitosan and sludges samples. Three samples of the differently formed

Table 5
Signification of regression coefficients of the studied factors

Coefficient name	Value	SD	*t*.exp	*P*-value (%)
		pH (Y_1)		
a_0	8.618	0.020	424.682	<0.01[a]
a_1	–0.034	0.024	–1.380	23.97
a_2	–0.150	0.024	–6.211	0.34[b]
a_3	0.067	0.024	2.760	5.08
a_4	0.083	0.024	3.450	2.60[c]
a_5	0.500	0.024	20.702	<0.01[a]
a_6	0.050	0.024	2.070	10.72
a_7	0.000	0.024	0.000	100.00
a_8	–0.034	0.024	–1.380	23.97
a_9	0.000	0.024	0.000	100.00
		COD (Y_2)		
b_0	736.656	20.332	36.231	<0.01[a]
b_1	88.415	24.200	3.654	2.17[c]
b_2	–11.585	24.200	–0.479	65.71
b_3	88.415	24.200	3.654	2.17[c]
b_4	138.415	24.200	5.720	0.46[b]
b_5	–111.585	24.200	–4.611	0.99[b]
b_6	138.415	24.200	5.712	0.46[b]
b_7	–11.585	24.200	–0.479	65.71
b_8	38.415	24.200	1.587	18.76
b_9	–111.585	24.200	–4.611	0.99[b]
		SM (Y_3)		
c_0	19.882	0.434	45.827	<0.01[a]
c_1	–0.125	0.516	–0.242	82.06
c_2	–0.375	0.516	–0.726	50.79
c_3	1.458	0.516	2.824	4.76
c_4	–0.042	0.516	–0.081	93.96
c_5	–1.875	0.516	–3.631	2.21[c]
c_6	1.042	0.516	2.017	11.39
c_7	–1.208	0.516	–2.340	7.94
c_8	–1.625	0.516	–3.147	3.46[c]
c_9	1.125	0.516	2.179	9.49
		λ (Y_4)		
d_0	11,789.412	14.390	819.304	<0.01[a]
d_1	15.000	17.127	0.876	43.10
d_2	61.667	17.127	3.601	2.30[c]
d_3	16.667	17.127	0.973	38.60
d_4	–25.000	17.127	–1.460	21.80
d_5	–206.667	17.127	–12.067	<0.01[a]
d_6	31.667	17.127	1.849	13.80
d_7	–6.667	17.127	–0.389	71.70
d_8	–63.333	17.127	–3.698	2.10[c]
d_9	116.667	17.127	6.812	0.20[b]
		[Cl] (Y_5)		
e_0	4,867.706	36.224	134.380	<0.01[a]
e_1	–133.167	43.115	–3.089	3.70[c]
e_2	–50.250	43.115	–1.165	30.90
e_3	–79.833	43.115	–1.852	13.80
e_4	56.250	43.115	1.305	26.20
e_5	73.917	43.115	1.714	16.20
e_6	–91.667	43.115	–2.126	10.10
e_7	–210.000	43.115	–4.871	0.08[b]
e_8	–74.000	43.115	–1.716	16.10
e_9	–50.250	43.115	–1.165	30.90

[a]High ($P < 0.01\%$); [b]medium ($P < 0.1\%$); [c]low ($P < 5\%$) significance, respectively.
SD – standard deviation.

sludge were visualized using SEM and results are illustrated in Fig. 2:

- SEM image of chitosan only;
- SEM image of dried sludge only;
- SEM image of the sludge formed when chitosan is used as coagulant;
- SEM image of sludge formed when aluminium sulphate is used as coagulant;

From SEM images (Figs. 2a–d), chitosan only reveals a structure composed of interconnected and porous fibers integrated into an amorphous matrix. Also, it is clear that dried sludge flocs are in the amorphous phase, fluffy with poorly defined geometry. Flocs of sludges generated from wastewater treatment with chitosan or $Al_2(SO_4)_3$ are homogeneous and smooth. Besides, there is no big difference between the flocs of sludge formed with chitosan or $Al_2(SO_4)_3$. However, the flocs aggregated with chitosan appeared like crystals and are more compact, sturdy and non-porous showing a strong colloid bridging. The compact agglomeration of colloids with chitosan can be induced by hydrogen bonds and Van der Waals forces. Renault et al. [26], reported that positively charged cationic macromolecules can destabilize the negative colloidal suspension by charge neutralization as well as by bridge formation. In addition, sludge may be disposed of with a lower environmental impact than common metal, which makes chitosan more advantageous than aluminium salt. It is also considered a good green alternative to a chemical coagulants. After the coagulation–flocculation, a biological treatment is set up, a minimum suspended matters, as well as the concentration of [Cl] and a satisfying abatement of COD, are required for the feasibility of the next step, that's why the chitosan was selected as a coagulant for further experiments. That's why the chitosan was selected as a coagulant for further experiments.

The six significant factors selected (X_2, X_4, X_5, X_6, X_7 and X_9) for the CF process were used to model and optimize responses by using response surface methodology (RSM) while the other remaining factors were kept constant at 100% chitosan, mixing rate of coagulant = 300 rpm and stirring time of flocculent = 2 min.

3.2. Response surface methodology

Khuri and Siuli [39] defined RSM as a group of mathematical and statistical techniques used in the development of an adequate functional relationship between a response of interest "Y" and a number of associated control (or input) variables denoted by $X_1, X_2, \ldots, X_n$.

3.2.1. Modelling of the chosen responses

3.2.1.1. Doehlert matrix

In this step, the Doehlert design is applied for the resulted continuous factors (X_2, X_4, X_5, X_6, X_7 and X_9). It is built by 46 experiments including four repeated centered points as shown in Table 6.

3.2.1.2. Factors signification

To find out the relation between the response variables and the most influencing factors on the process, the RSM was applied through developing polynomial regressions [40]. The predicted response was calculated using a polynomial model of second-order (Eq. (2)) to describe the relationship between relevant variables, their interaction and responses. Eq. (2) below represents the theoretical polynomial model:

$$Y_i = \beta_0 + \sum_i \beta_i X_i + \sum_{ij,i\neq j} \beta_{ij} X_i X_j + \sum_{ii} \beta_{ii} X_i^2 \quad (2)$$

where Y_{cal}: the predicted response; β_0: intercept; β_i: linear coefficients; β_{ii}: square coefficients; β_{ij}: interaction coefficients; X_i, X_j: independent variables.

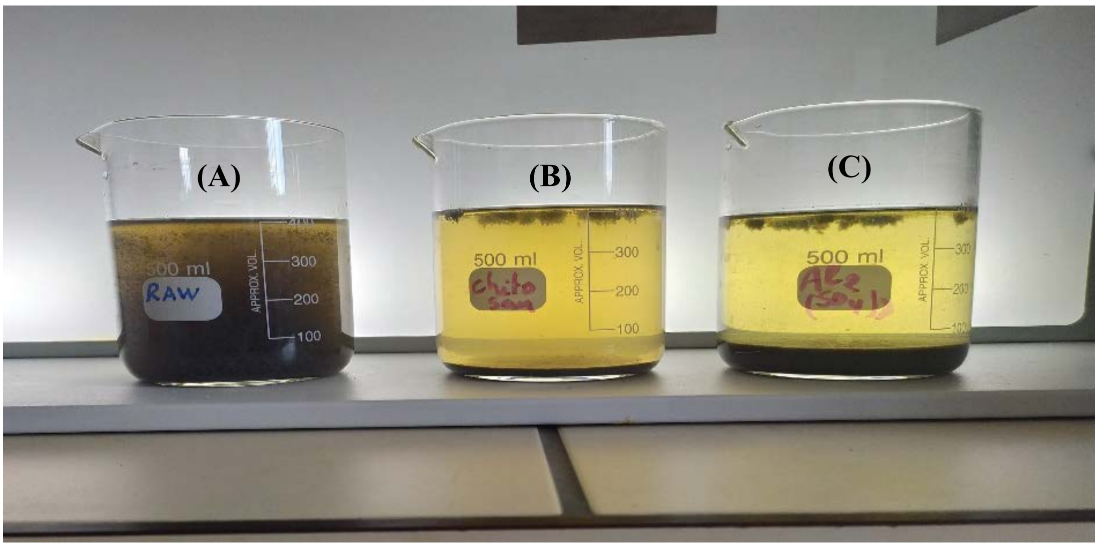

Fig. 1. Appearance of tannery wastewater before and after treatment by coagulation–flocculation (a) raw wastewater, (b) 100% chitosan, and (c) 100% aluminium sulphate.

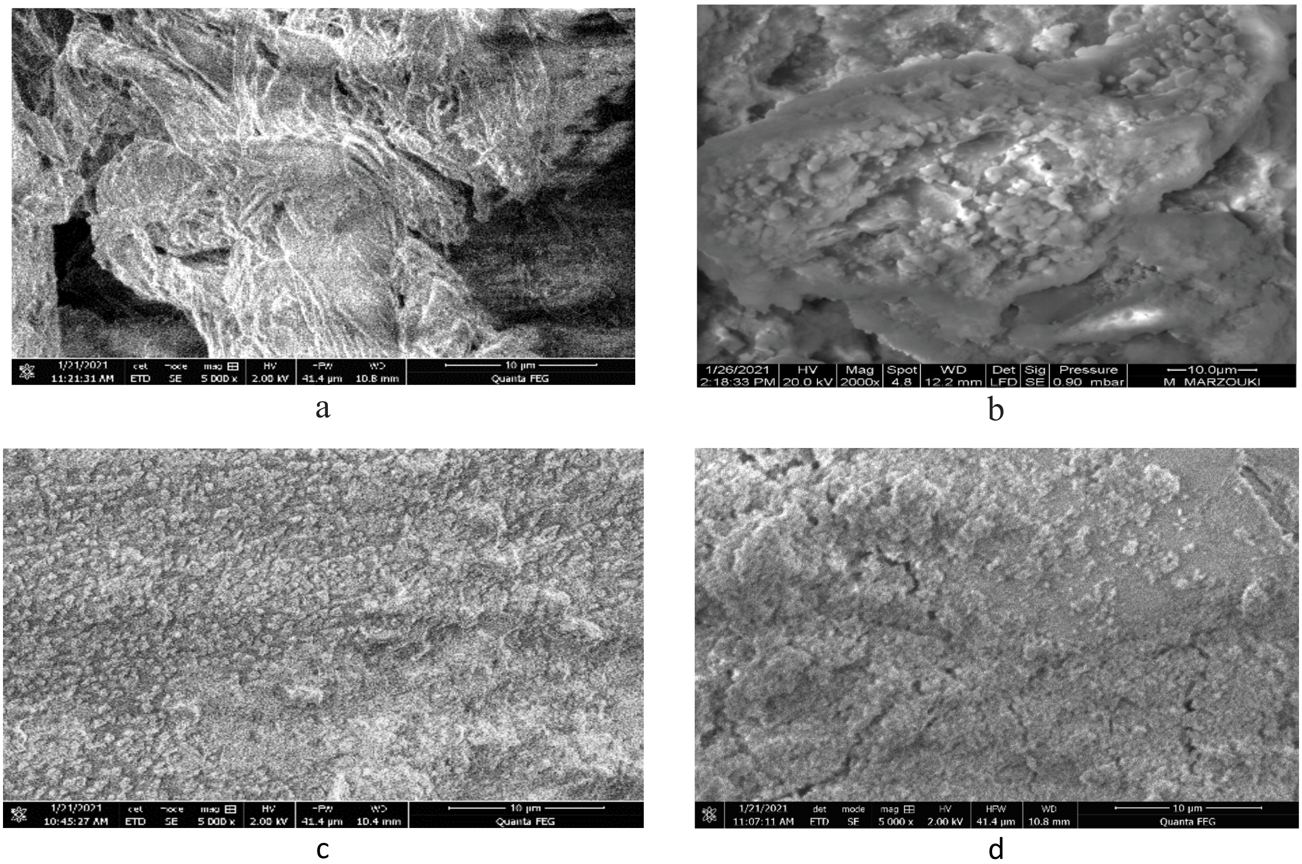

Fig. 2. (a) Chitosan only, (b) settled sludge only, (c) sludge formed with chitosan, and (d) sludge formed with $Al_2(SO_4)_3$, SEM scale (10 μm).

Table 7 shows the regression coefficients of the factors and interactions for the chosen responses at a significance of *P*-value of 0.05.

The application of the statistical student test induces to the resulted Eqs. (3)–(5) which correspond to the obtained models for the responses pH, COD and SM, respectively:

- pH response (Y_1):

$$Y_1 = 8.65 + 0.755X_5 - 0.22X_6^2 - 0.148X_9^2 - 0.569X_5X_7 - 0.245X_2X_5 + 0.942X_2X_9 + 0.942X_2X_7 + 0.261X_4X_7 - 0.306X_5X_7 + 0.273X_2X_9 - 0.386X_6X_9 - 0.316X_7X_9 \quad (3)$$

- COD response (Y_2):

$$Y_2 = 1{,}048.9 + 175.519X_5 - 570.949X_5^2 + 624.395X_4X_5 - 511.712X_2X_6 - 614.926X_7X_9 \quad (4)$$

- SM response (Y_3):

$$Y_3 = 12.125 + 12.916X_5^2 \quad (5)$$

3.2.1.3. Residual analysis

Fig. 3 shows the correlation between the modelled and observed values for pH, COD and SM. Graphically there is a good correlation between the predicted and observed values of the three response variables as explicitly reflected by a good agreement providing little evidence of lack-of-fit. That confirms that the three models of the chosen responses are moderately valid and to confirm this validity, an analysis of variance (ANOVA) is applied.

3.2.1.4. Analysis of variance

The ANOVA analysis is based on the comparison of the variance in the model established by the report to the variance of the residue, through the test of "Fisher Snedecor". For the model to be very significant at 95%, it is necessary that: $F_{exp} >> F_{\alpha}, \nu_{mod}, \nu_{res}$, where $\alpha = 0.05$.

Table 8 summarizes the ANOVA of the developed models for the chosen responses pH, COD, SM. In fact, the values of the ratio between the means squares of the lack-of-fit and pure error (8.872, 0.976 and 2.369, respectively) are inferior to the tabulated values $F_{32, 3, 0.05} = 8.60$, $F_{37, 3, 0.05} = 8.59$ and $F_{41, 3, 0.05} = 8.58$, respectively. Consequently, the three postulated models are valid.

In addition, the values of the ratio between the regression and residuals means squares (18.316, 33.187 and 51.206, respectively) are higher to the tabulated values $F_{10, 35, 0.05} = 2.11$ $F_{5, 40, 0.05} = 2.45$ and $F_{1, 44, 0.05} = 4.06$. So the established models are predictive. Consequently, all coefficients used

Table 6
Doehlert matrix design including the observed responses

N°. Exp.	Factors						Observed responses				
	X_2	X_4	X_5	X_6	X_7	X_9	Y_1	Y_2	Y_3	Y_4	Y_5
1	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.8	682	16.5	11,528	4,970
2	–1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.8	818	13.0	11,828	4,615
3	0.5000	0.8660	0.0000	0.0000	0.0000	0.0000	8.8	1,091	12.5	11,890	5,325
4	–0.5000	–0.8660	0.0000	0.0000	0.0000	0.0000	8.8	954	9.0	11,860	4,793
5	0.5000	–0.8660	0.0000	0.0000	0.0000	0.0000	8.7	1,091	20.0	11,720	3,905
6	–0.5000	0.8660	0.0000	0.0000	0.0000	0.0000	8.9	545	14.0	11,240	4,615
7	0.5000	0.2887	0.8165	0.0000	0.0000	0.0000	9.0	900	13.0	11,500	4,793
8	–0.5000	–0.2887	–0.8165	0.0000	0.0000	0.0000	8.2	439	20.0	11,660	5,325
9	0.5000	–0.2887	–0.8165	0.0000	0.0000	0.0000	8.0	600	20.0	11,950	4,935
10	0.0000	0.5774	–0.8165	0.0000	0.0000	0.0000	8.1	400	20.0	12,880	4,331
11	–0.5000	0.2887	0.8165	0.0000	0.0000	0.0000	9.6	1,000	35.5	11,640	4,899
12	0.0000	–0.5774	0.8165	0.0000	0.0000	0.0000	9.3	300	20.0	11,640	4,615
13	0.5000	0.2887	0.2041	0.7906	0.0000	0.0000	8.7	750	11.8	11,980	4,899
14	–0.5000	–0.2887	–0.2041	–0.7906	0.0000	0.0000	8.5	533	21.0	12,710	4,367
15	0.5000	–0.2887	–0.2041	–0.7906	0.0000	0.0000	8.6	1,067	17.5	12,670	4,615
16	0.0000	0.5774	–0.2041	–0.7906	0.0000	0.0000	8.4	585	22.0	11,900	5,148
17	0.0000	0.0000	0.6124	–0.7906	0.0000	0.0000	9.0	900	12.0	11,590	4,793
18	–0.5000	0.2887	0.2041	0.7906	0.0000	0.0000	8.5	989	15.6	11,870	5,148
19	0.0000	–0.5774	0.2041	0.7906	0.0000	0.0000	8.5	732	18.0	11,870	4,800
20	0.0000	0.0000	–0.6124	0.7906	0.0000	0.0000	8.2	533	17.0	12,620	4,438
21	0.5000	0.2887	0.2041	0.1581	0.7746	0.0000	9.6	689	12.0	12,030	4,615
22	–0.5000	–0.2887	–0.2041	–0.1581	–0.7746	0.0000	8.4	857	19.0	12,870	4,793
23	0.5000	–0.2887	–0.2041	–0.1581	–0.7746	0.0000	8.2	1,286	8.0	12,600	4,864
24	0.0000	0.5774	–0.2041	–0.1581	–0.7746	0.0000	8.3	732	22.5	12,030	5,040
25	0.0000	0.0000	0.6124	–0.1581	–0.7746	0.0000	9.4	900	17.5	11,530	5,183
26	0.0000	0.0000	0.0000	0.6325	–0.7746	0.0000	8.7	954	12.0	11,700	4,615
27	–0.5000	0.2887	0.2041	0.1581	0.7746	0.0000	8.4	1,020	16.0	11,930	4,828
28	0.0000	–0.5774	0.2041	0.1581	0.7746	0.0000	8.6	1,073	12.8	12,166	4,780
29	0.0000	0.0000	–0.6124	0.1581	0.7746	0.0000	8.1	800	22.5	12,410	4,615
30	0.0000	0.0000	0.0000	–0.6325	0.7746	0.0000	8.6	954	14.0	12,000	4,793
31	0.5000	0.2887	0.2041	0.1581	0.1291	0.7638	8.8	723	10.9	11,870	4,438
32	–0.5000	–0.2887	–0.2041	–0.1581	–0.1291	–0.7638	8.5	857	14.0	12,790	5,148
33	0.5000	–0.2887	–0.2041	–0.1581	–0.1291	–0.7638	8.2	1,296	8.5	12,650	4,901
34	0.0000	0.5774	–0.2041	–0.1581	–0.1291	–0.7638	8.3	585	21.0	11,850	4,793
35	0.0000	0.0000	0.6124	–0.1581	–0.1291	–0.7638	9.0	857	18.5	12,020	5,041
36	0.0000	0.0000	0.0000	0.6325	–0.1291	–0.7638	8.7	545	17.0	11,830	4,615
37	0.0000	0.0000	0.0000	0.0000	0.6455	–0.7638	8.6	1,363	16.5	11,820	4,828
38	–0.5000	0.2887	0.2041	0.1581	0.1291	0.7638	8.5	970	20.0	11,370	4,260
39	0.0000	–0.5774	0.2041	0.1581	0.1291	0.7638	8.6	1,056	13.5	11,998	4,872
40	0.0000	0.0000	–0.6124	0.1581	0.1291	0.7638	8.2	400	20.0	12,910	4,580
41	0.0000	0.0000	0.0000	–0.6325	0.1291	0.7638	8.6	818	13.5	11,600	4,544
42	0.0000	0.0000	0.0000	0.0000	–0.6455	0.7638	8.8	1,227	12.5	11,940	4,615
43	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.6	975	10.0	11,987	4,923
44	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.7	1,000	11.0	12,350	4,970
45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.7	1,230	15.2	12,410	4,559
46	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	8.6	990	12.3	11,740	4,810

Table 7
Significance of regression coefficients for the chosen responses

Coefficient name	Value	SD	*t*.exp	*P*-value (%)
		pH (Y_1)		
a'_0	8.650	0.029	299.640	<0.01[a]
a'_2	0.021	0.022	0.980	40.00
a'_4	0.054	0.022	2.460	9.00
a'_5	0.755	0.022	34.610	<0.01[a]
a'_6	–0.038	0.022	–1.760	17.60
a'_7	0.015	0.022	0.680	54.90
a'_9	0.022	0.022	1.000	39.20
a'_{22}	0.150	0.050	3.000	5.60
a'_{44}	0.150	0.050	3.000	5.60
a'_{55}	–0.000	0.047	–0.000	100.00
a'_{66}	–0.220	0.045	–4.920	1.45[c]
a'_{77}	–0.047	0.043	–1.090	35.70
a'_{99}	–0.148	0.041	–3.570	3.59[c]
a'_{24}	0.000	0.067	0.000	100.00
a'_{25}	–0.245	0.075	–3.290	4.48[c]
a'_{45}	0.000	0.075	0.000	100.00
a'_{26}	0.126	0.077	1.630	20.10
a'_{46}	0.183	0.077	2.360	9.90
a'_{56}	–0.181	0.077	–2.330	10.10
a'_{27}	0.942	0.079	11.950	0.08[a]
a'_{47}	0.261	0.079	3.310	4.41[c]
a'_{57}	–0.306	0.079	–3.880	2.88[c]
a'_{67}	–0.237	0.079	–3.000	5.60
a'_{29}	0.273	0.080	3.420	4.03[c]
a'_{49}	–0.006	0.080	–0.080	94.00
a'_{59}	–0.178	0.080	–2.240	11.00
a'_{69}	–0.386	0.080	–4.850	1.51[c]
a'_{79}	–0.316	0.080	–3.960	2.71[c]
		COD (Y_2)		
b'	1,048.900	88.748	11.820	<0.01[a]
b'_2	75.291	67.087	1.120	27.60
b'_4	–117.038	67.085	–1.740	9.50
b'_5	175.519	67.087	2.620	1.68[c]
b'_6	–48.291	67.084	–0.720	48.70
b'_7	–11.894	67.087	–0.180	85.60
b'_9	–33.787	67.084	–0.500	62.60
b'_{22}	–298.900	153.716	–1.940	6.50
b'_{44}	–71.671	153.725	–0.470	65.10
b'_{55}	–570.949	144.921	–3.940	0.10[b]
b'_{66}	–272.089	137.475	–1.980	6.10
b'_{77}	–1.594	131.632	–0.010	98.70
b'_{99}	–95.930	126.980	–0.760	46.60
b'_{24}	236.201	204.960	1.150	26.40
b'_{25}	–243.345	229.148	–1.060	30.30
b'_{45}	624.395	229.128	2.730	1.34[c]
b'_{26}	–511.712	238.127	–2.150	4.35[c]
b'_{46}	178.990	238.106	0.750	46.80

(Continued)

Table 7 Continued

Coefficient name	Value	SD	*t*.exp	*P*-value (%)
		COD (Y_2)		
b'_{34}	–107.286	238.129	–0.450	66.10
b'_{27}	–409.789	242.504	–1.690	10.50
b'_{47}	–26.279	242.483	–0.110	91.10
b'_{57}	–34.671	242.505	–0.140	88.30
b'_{67}	–31.448	242.497	–0.130	89.40
b'_{29}	–298.467	244.955	–1.220	23.70
b'_{49}	99.593	244.934	0.410	69.10
b'_{59}	280.759	244.956	1.150	26.60
b'_{69}	298.466	244.947	1.220	23.70
b'_{79}	–614.926	244.955	–2.510	2.09[c]
		SM (Y_3)		
c'_0	12.125	2.320	5.230	<0.01[a]
c'_2	–3.064	1.754	–1.750	9.4
c'_4	1.720	1.754	0.980	34.2
c'_5	–0.682	1.754	–0.390	70.3
c'_6	–1.034	1.754	–0.590	56.9
c'_7	0.160	1.754	0.090	92.5
c'_9	–0.556	1.754	–0.320	75.2
c'_{22}	2.625	4.019	0.650	52.9
c'_{44}	1.458	4.019	0.360	72.1
c'_{55}	12.916	3.789	3.410	0.316[b]
c'_{66}	4.180	3.594	1.160	25.9
c'_{77}	2.312	3.441	0.670	51.7
c'_{99}	2.415	3.320	0.730	48.2
c'_{24}	–7.217	5.358	–1.350	19.2
c'_{25}	–11.226	5.991	–1.870	7.4
c'_{45}	2.593	5.990	0.430	67.3
c'_{26}	5.344	6.225	0.860	40.6
c'_{46}	–6.243	6.225	–1.000	33.1
c'_{56}	10.496	6.225	1.690	10.6
c'_{27}	9.076	6.340	1.430	16.6
c'_{47}	–5.657	6.339	–0.890	38.8
c'_{57}	–4.237	6.340	–0.670	51.9
c'_{67}	4.458	6.340	0.700	49.7
c'_{29}	0.731	6.404	0.110	90.7
c'_{49}	–4.781	6.403	–0.750	47.1
c'_{59}	–3.019	6.404	–0.470	64.7
c'_{69}	–0.766	6.404	–0.120	90.2
c'_{79}	–0.006	6.404	–0.000	99.5
		λ (Y_4)		
d'_0	12,121.750	157.870	76.780	<0.01[a]
d'_2	22.857	119.339	0.190	85.30
d'_4	–1,271.098	119.334	–10.650	0.12[b]
d'_5	911.045	119.338	7.630	0.36[b]
d'_6	–103.554	119.334	–0.870	45.20
d'_7	–58.184	119.338	–0.490	65.90
d'_9	–138.762	119.333	–1.160	33.00

d'_{22}	–443.750	273.440	–1.620	20.30
d'_{44}	–444.443	273.456	–1.630	20.20
d'_{55}	–3,359.810	257.795	–13.030	0.06[a]
d'_{66}	896.707	244.550	3.670	3.35[c]
d'_{77}	566.657	234.155	2.420	9.30
d'_{99}	281.640	225.881	1.250	30.20
d'_{24}	456.120	364.597	1.250	30.00
d'_{25}	–424.595	407.623	–1.040	37.60
d'_{45}	8,287.769	407.587	20.330	0.02[a]
d'_{26}	37.918	423.595	0.090	93.20
d'_{46}	–1,522.814	423.559	–3.600	3.54[c]
d'_{56}	–1,410.282	423.599	–3.330	4.33[c]
d'_{27}	172.971	431.382	0.400	71.20
d'_{47}	–1,486.419	431.345	–3.450	3.96[c]
d'_{57}	–773.150	431.384	–1.790	17.00
d'_{67}	1,980.837	431.369	4.590	1.78[c]
d'_{29}	322.928	435.742	0.740	51.5
d'_{49}	–1,276.604	435.705	–2.930	6.0
d'_{59}	–1,740.563	435.743	–3.990	2.65[c]
d'_{69}	1,875.210	435.728	4.300	2.14[c]
d'_{79}	1,302.480	435.741	2.990	5.7
		[Cl] (Y_5)		
e'_0	4,815.500	91.855	52.420	<0.01[a]
e'_2	–12.536	69.436	–0.180	86.2
e'_4	521.787	69.434	7.510	0.381[b]
e'_5	–80.489	69.436	–1.160	33.1
e'_6	–568.041	69.433	–8.180	0.288[b]
e'_7	–109.253	69.436	–1.570	21.3
e'_9	–220.076	69.433	–3.170	4.91[c]
e'_{22}	–23.000	159.098	–0.140	88.9
e'_{44}	–200.512	159.108	–1.260	29.7
e'_{55}	56.886	149.996	0.380	72.6
e'_{66}	–980.562	142.289	–6.890	0.504[b]
e'_{77}	186.038	136.241	1.370	26.6
e'_{99}	–27.396	131.427	–0.210	84.1
e'_{24}	922.344	212.137	4.350	2.08[c]
e'_{25}	–152.212	237.171	–0.640	56.9
e'_{45}	665.134	237.151	2.800	6.6
e'_{26}	–611.832	246.465	–2.480	8.8
e'_{46}	2,916.656	246.444	11.830	0.0860[a]
e'_{56}	–808.228	246.467	–3.280	4.50[c]
e'_{27}	–362.101	250.995	–1.440	24.5
e'_{47}	–1,037.951	250.974	–4.140	2.40[c]
e'_{57}	128.554	250.997	0.510	64.4
e'_{67}	–344.752	250.988	–1.370	26.3
e'_{29}	157.454	253.532	0.620	58.0
e'_{49}	–893.440	253.511	–3.520	3.73[c]
e'_{59}	115.190	253.533	0.450	67.9
e'_{69}	–227.496	253.524	–0.900	43.8
e'_{79}	315.464	253.532	1.240	30.2

[a]High ($P < 0.01\%$); [b]medium ($P < 0.1\%$); [c]low ($P < 5\%$) significance, respectively.
SD – standard deviation.

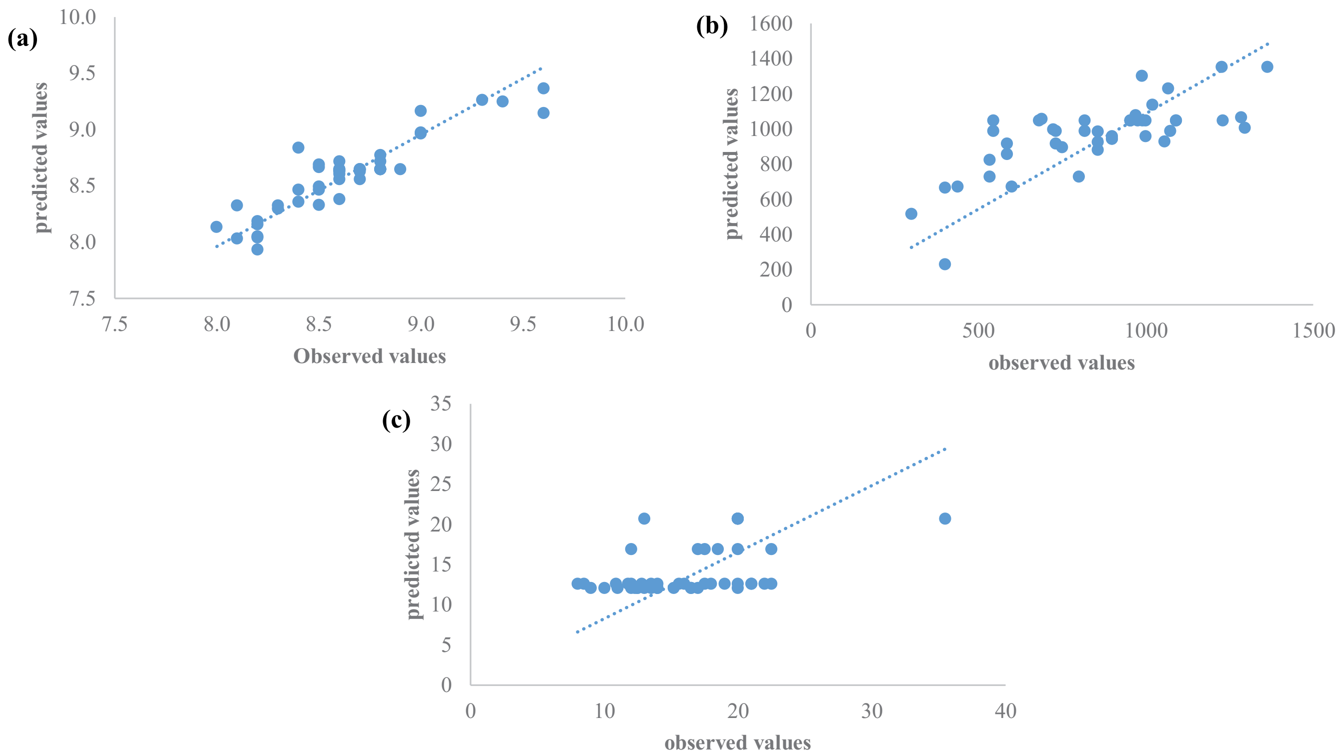

Fig. 3. The distribution of the calculated vs. observed values for the three responses (a) pH, (b) COD, and (c) SM.

Table 8
Analysis of variance for pH, COD and SM responses models

Source of variance	SS	DF	MS	Ratio	Signification (%)
			pH (Y_1)		
Regression	5.005	10	0.500	18.316	<0.01***
Residuals	0.956	35	0.027		
Lack-of-fit	0.946	32	0.030	8.872	5.0
Pure error	0.010	3	0.003		
Total	5.961	45			
			COD (Y_2)		
Regression	2.382E+06	5	4.760E+05	33.187	<0.01***
Residuals	5.742E+05	40	1.440E+04		
Lack-of-fit	5.302E+05	37	1.430E+04	0.976	60.70
Pure error	4.403E+04	3	1.470E+04		
Total	2.956E+06	45			
			SM (Y_3)		
Regression	592.930	1	592.930	51.206	<0.01***
Residuals	509.491	44	11.579		
Lack-of-fit	494.224	41	12.054	2.369	26.20
Pure error	15.267	3	5.089		
Total	1,102.421	45			

SS – Sum of squares; DF – Degree of freedom; MS – Mean squares.

for the postulated models have a significant effect on the chosen responses (pH, COD and SM).

3.3. Analysis of results related to conductivity and chloride concentration responses

The polynomial regression equation related to the response Y_4 (conductivity) is given by Eq. (6):

$$\begin{aligned}Y_{4\text{cal}} &= 12{,}121.75 - 1{,}271.098X_4 + 911.045X_5 + 3{,}359.81X_5^2 \\ &+ 896.707X_6^2 + 8{,}287.769X_4X_5 - 1{,}522.814X_4X_6 \\ &- 1{,}410.282X_5X_6 - 1{,}486.419X_4X_3 + 1{,}980.837X_6X_7 \\ &- 1{,}740.563X_5X_9 + 1{,}875.210X_6X_9 \end{aligned} \quad (6)$$

The polynomial regression equation related to the response Y_5 (Cl concentration) is given by Eq. (7):

$$\begin{aligned}Y_{5\text{cal}} &= 4{,}815.5 + 521.787X_4 - 568.041X_6 - 220.076X_9 \\ &+ 980.562X_6^2 + 922.344X_2X_4 + 2{,}916.656X_4X_6 \\ &- 808.228X_5X_6 - 1{,}037.951X_4X_7 - 893.44X_4X_9 \end{aligned} \quad (7)$$

- Analysis of variance and residue for conductivity and Cl concentration

It is noted that these two models [Eqs. (6) and (7)] are well predictive but unfortunately not valid. There is a significant effect of lack-of-fit according to the comparison between the calculated values and the tabulated Fisher values, which reflect a significant systematic error. Therefore, the multi-response optimization method by using desirability is required here.

3.4. Multi-response optimization using desirability

The focus of the optimal conditions for a system of multiple responses, in which some of them have a predictive postulated model but not valid, needs to use the simultaneous optimization method by using the desirability functions. Desirability is an effective method for the industry for the optimization of multiple quality characteristic problems. This method makes use of a global objective function, D, called the global desirability function and transforms an estimated response into a scale-free value (d_i) called an individual desirability function. The global desirability function is the geometric mean of the individual desirability functions and it is given by Eq. (8) [41]:

$$D = \sqrt[m]{\prod_i^m d_i} \quad (8)$$

where m is the number of the chosen responses (in our case 5 responses: pH, COD, SM, conductivity λ and [Cl]. The desirable ranges are from zero to one (least to most desirable, respectively). The factor settings with maximum total desirability are considered to be the optimal parameter condition [42]. In numerical optimization, the desired goal for each response is chosen from the menu. The possible goals are: maximize, minimize, target, within the range and none [43]. By using the NemrodW software (LPRAI, Marseille-French, version 2000) the setting of each response interval is done with minimum, maximum and target level [44]. Finally, the desirability function gives us a compromise of all these targets that we would like to satisfy by combining these numerical data. Fig. 4 shows the shape of the curve for each response with the chosen target. For Fig. 4a, the target domain is between 8 and 9.6, out of this domain, the desirability is 0%. For 4b–e, when the desirability is 100%, the target values are less than 600 mg O_2/L, 13 mg/L and 3,000 mg/L for the responses COD, SM, conductivity, respectively. The predicted optimal conditions (Table 8) allow obtaining the best abatement around 8.6 for pH (D1: 100%), 592 mg O_2/L for COD (D2: 100%), 12.8 mg/L for SM (D3: 100%), 12,710 µS/cm for conductivity (D4: 100%) and 2,889 mg/L for [Cl] (D5: 100%). This optimal response were given by the optimal CF conditions at an initial pH of 8.8, for the step of coagulation: coagulant dosage 612.8 mg/L, stirring speed 6 rpm and for the step of flocculation: Zetag dosage 5.6 mg/L, stirring speed 43 rpm and 22 min for settling time. This result reveals that all the targets are significantly satisfied.

In order to check these optimal conditions, a four times repeated tests are done. Table 9 resumes the obtained values: pH (Y_1) = 8.7 ± 0.1, COD (Y_2) = 599 ± 75 mg O_2/L, SM (Y_3) = 13.2 ± 1.3 mg/L, λ (Y_4) = 12,221 ± 502 µS/cm and [Cl] (Y_5) = 2,941 ± 108 mg/L. It is very clear that all predicted responses belong to the confidence intervals of the observed responses.

4. Conclusion

The present work deals with the use of biocoagulant (chitosan) as substitute for chemicals (sulphate aluminium) in the treatment of tannery wastewater using coagulation–flocculation. The optimization of the physical-chemical

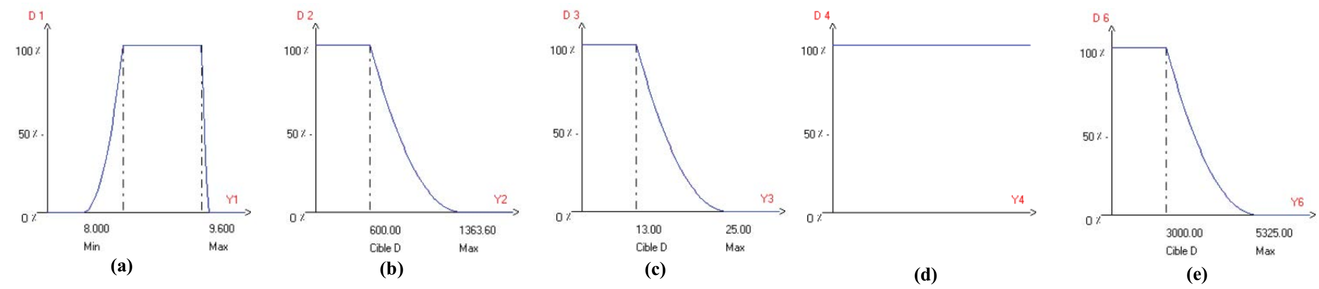

Fig. 4. Different desirability plots for each response: (a) pH, (b) COD, (c) SM, (d) conductivity (λ), and (e) [Cl].

Table 9
Predicted and observed optimal conditions

Predicted coordinates					Predicted responses				Observed responses		
Factors	Coded value	Factor name	Unit	Predicted value	Response	Unit	Value	d_i (%)	Response	Unit	Value
X_2	0.564	Coagulant dosage	mg/L	612.8	pH (Y_1)	–	8.6	100.00	pH (Y_1)	–	8.7 ± 0.1
X_4	0.555	Stirring speed step 1	rpm	6	COD (Y_2)	mg O_2/L	592	100.00	COD (Y_2)	mg O_2/L	599 ± 75
X_5	–0.204	Initial pH	–	8.8							
X_6	0.435	Zetag dosage	mg/L	5.6	SM (Y_3)	mg/L	12.8	100.00	SM (Y_3)	mg/L	13.2 ± 1.3
X_7	0.335	Stirring speed step 2	rpm	43	λ (Y_4)	µS/cm	12,710	100.00	λ (Y_4)	µS/cm	12,221 ± 502
X_9	0.187	Settling time	min	22	[Cl] (Y_5)	mg/L	2,889	100.00	[Cl] (Y_5)	mg/L	2,941 ± 108

treatment of tannery effluent was based on experimental design and response surface methodology. The proposed approach is consisting of an initial screening using Plackett–Burman method to identify the most sensitive parameters followed subsequently by modelling the relationship between these parameters and performances indicators via the Doehlert method. A comparison between chemical and biocoagulant efficiency is also evaluated. The elaborated response model has been tested using the analysis of variance (ANOVA). The target responses, that is, pH: 8.6, COD: 592 mg O_2/L, SM: 12.8 mg/L and [Cl]: 2,889 mg/L were obtained with the following optimal conditions: dosage of chitosan = 612.8 mg/L, a stirring speed of 6 rpm at an initial pH of 8.8, and 5.6 mg/L of flocculant with a stirring speed of 43 rpm followed by a settling time of 22 min. The most significant abatements obtained for COD, SM and [Cl] are 68.90%, 95.24% and 39.72% respectively. These removal rates could have an interesting impact for conventional biological treatment and sludge managing. The results suggest also that chitosan could be used as substitute for aluminium sulphate while presenting the advantages of being eco-friendly environmentally and low-cost energy consumption.

References

[1] S.L. Xu, X.L. Niu, Z.S. Hou, C.H. Gao, J.M. Lu, Y.Y. Pang, M. Fang, Y. Lu, Y.J. Chen, K.S. Joshy, T.D. Li, J. Xu, A multifunctional gelatine–quaternary ammonium copolymer: an efficient material for reducing dye emission in leather tanning process by superior anionic dye adsorption, J. Hazard. Mater., 383 (2020) 121142, doi: 10.1016/j.jhazmat.2019.121142.

[2] Z. Song, C.J. Williams, R.G.J. Edyvean, Treatment of tannery wastewater by chemical coagulation, Desalination, 164 (2004) 249–259.

[3] F. Giaccherini, G. Munz, T. Dockhorn,C. Lubello, D. Ross, Carbon and energy footprint analysis of tannery wastewater treatment: a global overview, Water Resour. Ind., 17 (2019) 43–52.

[4] R. Boujelben, M. Ellouze, S. Sayadi, Detoxification assays of Tunisian tannery wastewater under nonsterile conditions using the filamentous fungus *Aspergillus niger*, BioMed Res. Int., 2019 (2019) 9020178, dio: 10.1155/2019/9020178.

[5] C. Manjushree, M.G. Mostafa, K.B. Tapan, K.S. Ananda, Treatment of leather industrial effluents by filtration and coagulation processes, Water Resour. Ind., 3 (2013) 11–22.

[6] I. Ahmed, M. Habib, U. Habib, A. Hai, A.U. Khan, Analysis and treatment of tannery waste water by using combined filtration and coagulation treatment process, Proc. Pak. Acad. Sci.: B. Life Environ. Sci., 53 (2016) 179–183.

[7] S. Aber, D. Salari, M.R. Parsa, Employing the Taguchi method to obtain the optimum conditions of coagulation–flocculation process in tannery wastewater treatment, Chem. Eng. J., 162 (2010) 127–134.

[8] M. Gutterres, P.M. Aquim, J.B. Passos, J.O. Trierweiler, Water reuse in tannery beamhouse process, J. Cleaner Prod., 18 (2010) 1543–1550.

[9] M. Scholz, Chapter 7 – Coagulation and Flocculation, in: Wetlands for Water Pollution Control, Elsevier Science, The University of Salford, Salford, UK, 2016, pp. 37–46.

[10] Z. Bajza, P. Hitrec, M. Muic, Influence of different concentrations of $Al_2(SO_4)_3$ and anionic polyelectrolytes on tannery wastewater flocculation, Desalination, 171 (2005) 13–20.

[11] G.M. Ayoub, A. Hamzeh, L. Semerjian, Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption, Desalination, 273 (2011) 359–365.

[12] C.Y. Teh, P.M. Budiman, K.P.Y. Shak, T. Wu, Recent advancement of coagulation−flocculation and its application in wastewater treatment, Ing. Eng. Chem. Res., 55 (2016) 4363–4389.

[13] S. Verma, B. Prasad, I.M. Mishra, Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics, J. Hazard. Mater., 178 (2010) 1055–1064.

[14] W.L. Ang, A.W. Mohammad, Y.H. Teow, A. Benamor, N. Hilal, Hybrid chitosan/$FeCl_3$ coagulation–membrane processes: performance evaluation and membrane fouling study in removing natural organic matter, Sep. Purif. Technol., 152 (2015) 23–31.

[15] E. Marañón, L. Castrillón, Y. Fernández-Nava, A. Fernández-Méndez, A. Fernández-Sánchez, Coagulation–flocculation as a pretreatment process at a landfill leachate nitrification–denitrification plant, J. Hazard. Mater., 156 (2008) 538–544.

[16] A.Y. Zahrim, A. Nasimah, N. Hilal, Coagulation/flocculation of lignin aqueous solution in single stage mixing tank system: modeling and optimization by response surface methodology, J. Environ. Chem. Eng., 3 (2015) 2145–2154.

[17] M. Nigam, S. Rajoriya, S.R. Singh, P. Kumar, Adsorption of Cr(VI) ion from tannery wastewater on tea waste: kinetics, equilibrium and thermodynamics studies, J. Environ. Chem. Eng., 7 (2019) 103188, doi: 10.1016/j.jece.2019.103188.

[18] S. Rajoriya, A. Haquiqi, B. Chauhan, G. Tyagi, A.S. Pundir, A.K. Jain, D. Agarwal, Adsorption studies on the removal of hexavalent chromium (Cr(VI)) from aqueous solution using black gram husk, J. Environ. Treat. Tech., 8 (2020) 1144–1150.

[19] A.Y. Zahrim, C. Tizaoui, N. Hilal, Removal of highly concentrated industrial grade leather dye: study on several flocculation and sand filtration parameters, Sep. Sci. Technol., 46 (2011) 883–892.

[20] H. Zemmouri, M. Drouiche, A. Sayeh, H. Lounici, N. Mameri, Coagulation–flocculation test of Keddara's water dam using chitosan and sulfate aluminum, Procedia Eng., 33 (2012) 254–260.
[21] T.K.F.S.Freitas, V.M. Oliveira, M.T.F. de Souza, H.C.L. Geraldino, V.C. Almeida, S.L. Fávaro, J.C. Garcia, Optimization of coagulation–flocculation process for treatment of industrial textile wastewater using OKRA (*A. esculentus*) mucilage as natural coagulant, Ind. Crops Prod., 76 (2015) 538–544.
[22] J. Dotto, M.R. Fagundes-Klen, M.T. Veit, S.M. Palácio, R. Bergamasco, Performance of different coagulants in the coagulation/flocculation process of textile wastewater, J. Cleaner Prod., 208 (2019) 656–665.
[23] R. Yang, H.J. Li, M. Huang, H. Yang, A. Li, A review on chitosan-based flocculants and their applications in water treatment, Water Res., 95 (2016) 59–89.
[24] K. Kurita, Chitin and chitosan: functional biopolymers from marine crustaceans, Mar. Biotechnol., 8 (2006) 203–226.
[25] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of color from textile wastewaters, J. Environ. Manage., 93 (2012) 154–168.
[26] F. Renault, B. Sancey, P.-M. Badot, G. Crini, Chitosan for coagulation/flocculation processes – an eco-friendly approach, Eur. Polym. J., 45 (2009) 1337–1348.
[27] F.H. Chi, W.P. Cheng, Use of chitosan as coagulant to treat wastewater from milk processing plant, J. Polym. Environ., 14 (2006) 411–417.
[28] G. Durai, M. Rajasimman, Biological treatment of tannery wastewater – a review, J. Environ. Sci. Technol., 4 (2011) 1–17.
[29] S. Sivaprakasam, S. Mahadevan, S. Sekar, S. Rajakumar, Biological treatment of tannery wastewater by using salt-tolerant bacterial strains, Microb. Cell Fact., 7 (2008) 15, doi: 10.1186/1475-2859-7-15.
[30] T. Lundstedt, E. Seifert, L. Abramo, B. Thelin, Å. Nyström, J. Pettersen, R. Bergman, Experimental design and optimization, Chemom. Intell. Lab. Syst., 42 (1998) 3–40.
[31] M.A.Z. Mohd Remy Rozainy, M. Hasif, Syafalny, P. Puganeshwary, A. Afifi, Combination of chitosan and bentonite as coagulant agents in dissolved air flotation, APCBEE Procedia, 10 (2014) 229–234.
[32] S. Mansouri, N. Elhammoudi, S. Aboul-Hrouz, M. Mouiya, L. Makouki, A. Chham, A. Abourriche, H. Hannache, M. Oumam, Elaboration of novel adsorbent from Moroccan oil shale using Plackett–Burman design, Chem. Int., 4 (2018) 7–14.
[33] G. Bouazza, M. Assou, S. Souabi, E.H. Chatri, Modelling by the experimental design for color removal (absorbance at 254 nm) from tannery wastewater, Desal. Water Treat., 148 (2019) 324–328.
[34] H. Wei, B.Q. Gao, J. Ren, A. Li, H. Yang, Coagulation/Flocculation in dewatering of sludge: a review, Water Res., 143 (2018) 608–631.
[35] S. BinAhmed, G. Ayoub, M. Al-Hindi, F. Azizi, The effect of fast mixing conditions on the coagulation–flocculation process of highly turbid suspensions using liquid bittern coagulant, Desal. Water Treat., 53 (2014) 3388–3396.
[36] J. Mabrouki, A. Moufti, I. Bencheikh, K. Azoulay, Y. El Hamdouni, S. El Hajjaji, Optimization of the Coagulant Flocculation Process for Treatment of Leachate of the Controlled Discharge of the City Mohammedia (Morocco), International Conference on Advanced Intelligent Systems for Sustainable Development, M. Ezziyyani, Ed., Advanced Intelligent Systems for Sustainable Development (AI2SD'2019), AI2SD 2019. Lecture Notes in Electrical Engineering, Springer, Cham, 2020, pp. 200–212.
[37] Ö.B. Gökçek, S. Özdemir, Optimization of the coagulation–flocculation process for slaughterhouse wastewater using response surface methodology, Clean – Soil Air Water, 48 (2020) 200033 (1–12), doi: 10.1002/clen.202000033.
[38] G. Lofrano, S. Meriç, G.E. Zengin, D. Orhon, Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review, Sci. Total Environ., 461 (2013) 265–281.
[39] A.I. Khuri, M. Siuli, Response surface methodology, WIREs Comput. Stat., 2 (2010) 128–149.
[40] M. Khayet, A.Y. Zahrim, N. Hilal, Modelling and optimization of coagulation of highly concentrated industrial grade leather dye by response surface methodology, Chem. Eng. J., 167 (2011) 77–83.
[41] C. Cojocaru, M. Khayet, G. Zakrzewska-Trznadel, A. Jaworska, Modeling and multi-response optimization of pervaporation of organic aqueous solutions using desirability function approach, J. Hazard. Mater., 167 (2009) 52–63.
[42] M.A. Aounallah, I.B. Slimene-Debez, K. Djebali, D. Gharbi, M. Hammami, S. Azaiez, F. Limam, O. Tabbene, Enhancement of exochitinase production by *Bacillus licheniformis* AT6 strain and improvement of N-Acetylglucosamine production, Appl. Biochem. Biotechnol., 181 (2017) 650–666.
[43] M.J. Prakash, S. Manikandan, B. Priya, P. Gurumoorthi, Box-Behnken design based multi-response analysis and optimization of supercritical carbon dioxide extraction of bioactive flavonoid compounds from tea (*Camellia sinensis* L.) leaves, J. Food Sci. Technol., 52 (2013) 92–104.
[44] M. Mourabet, A. El Rhilassi, H. El Boujaady, M. Bennani-Ziatni, R. El Hamri, A. Taitai, Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology, J. Saudi Chem. Soc., 19 (2015) 603–615.