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ORIGINAL PAPER

Optimization of coag-flocculation processes of a newly synthesized quaternized oil palm empty fruit bunch cellulose by response surface methodology toward drinking water treatment process application

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Abstract An optimization of coagulation and flocculation of kaolin suspension by a newly synthesized quaternized oil palm empty fruit bunch cellulose denoted as a 9QC was investigated using the central composite design of the response surface methodology. The influences of coag-flocculant dosage, pH, and kaolin suspension on turbidity removal efficiency and sludge volume index responses were studied and assessed according to a 2^3 full factorial design. The developed quadratic models revealed that the overall optimum values to obtain the highest performance of the responses were 62.5 mg/L of coag-flocculant dosage, pH 7, and 1400 mg/L of kaolin concentration. The predicted optimum responses were found to be in close proximity to the observed responses. The coag-flocculating of river water using 9QC carried out at the optimum values showed encouraging results as compared to alum which is commonly used in drinking water treatment process.

Keywords Oil palm empty fruit bunch · Quaternized cellulose · Optimization · Turbidity removal efficiency · Sludge volume index

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Introduction

Water is a vital resource for sustaining human life and other living things, in fact, it is considered a basic human right (Jain 2011, 2012). The sources of water for human consumption are surface water, particularly from streams, rivers, lakes or oceans, and groundwater (Spellman 2009). These water sources are often subjected to contamination by various pollutants as a result of both natural and man-made activities which require proper water treatment strategies (Jain 2012). Diverse conventional and advanced water treatment processes have been developed for producing clean and safe water for consumption offering improved performance and cost-effective processes. Recently, Roy et al. (2015) have determined a simple, cheap, and efficient water treatment to remove arsenic from groundwater in augmentation of drinking water application. Dual treatment of conventional techniques consists of oxidation coagulation–filtration, and adsorption were found to be economically feasible and efficient compared to the others. Bani-Melhem et al. (2015) have investigated the performance of a non-conventional submerged membrane bioreactor system for gray water in promoting a high-quality fresh water with minimum pollutants in the environment.

The coag-flocculation process is one of the conventional technologies widely applied in the drinking water treatment process due to its low-cost and simplicity (Tzoupanos and Zouboulis 2008). It is a vital step in water treatment processes since the produced water that is deemed fit as drinking water must be visibly clear from the non-settling particles and turbid coloring. A variety of coag-flocculants have been used to remove contaminants from water while complying with the drinking water quality standard as well as its assertive rules and regulations. The inorganic salts

(e.g., aluminum sulfate or alum, ferrous sulfate) and polymer-based (e.g., polyaluminum chloride and polyferric chloride) coag-flocculants have been widely studied and used as conventional coag-flocculants in water and wastewater treatment process (Matilainen et al. 2010). These commercially available coag-flocculants are facing several drawbacks regarding their hazard to the environment, implications to human health, generating large sludge scale and declining cost benefit associated with synthetic polymer as the raw material price increases due to the rising price of oil (Renault et al. 2009). The research nowadays has thus acquired growing interest in the utilization of natural sources due to their environment-friendly and biodegradability properties (Lee et al. 2014). Natural-based coag-flocculants are non-toxic, moderately shear stable, generate no secondary pollution and locally available which make them inexpensive and safe alternatives for human and the environment (Bolto and Gregory 2007).

Tannin (Özacar and Şengil 2003), gum and mucilage (Al-Hamadani et al. 2011), and algal alginate (Devrimci et al. 2012) are some examples of the natural compounds explored for their potential applications in water treatment processes. Chitosan produced from deacetylation of chitin has also received greater attention as an eco-friendly coag-flocculant (Renault et al. 2009). The presence of primary amino groups makes this natural compound attractive, and as the chitin is the second most abundant biopolymer, it seems promising in terms of cost-effectiveness. Cellulose is another attractive natural source which is available in a larger quantity than chitin. It is the most abundant naturally occurring organic compound consisting of 40–60 wt% in dry wood and more than 90 % in raw cotton and flax, which covers one-third of advanced plants (Kamide 2005). Studies focusing on developing and modifying cellulose as a coag-flocculant are not new and have started as early as 1971 by Machida et al. (1971) who had grafted cellulose with polyacrylamide. Recently, a one-step homogenous modification method was reported (Zhu et al. 2015). Dicarboxyl cellulose from bamboo was synthesized via the Schiff base route which simplifies the complexity and heterogeneity of the traditional two-step method. Cellulose from cotton was also hydrolyzed and sulfonated with chlorosulfonic acid in dimethylformamide to obtain anionic flocculant for turbidity removal of kaolin suspension (Nourani et al. 2016). Although many reports on natural compounds in water and wastewater treatment can be found, there are very limited reports on the application of the cellulose-based coag-flocculants for the drinking water treatment process.

The isolation of cellulose from wastes such as oil palm biomass (OPB) is very attractive since they are abundantly available. These wastes are potential biomass feedstocks for the production of high value-added products such as fermentable sugar (Alkasrawi et al. 2016), bioethanol (Gurram et al. 2016), and biofuel (Alias et al. 2015); however, their applications are not fully explored for water treatment. The exploitation of OPB as cellulose raw material can also help in overcoming the disposal of solid waste issues which has lately become an environmental concern. The OPB such as oil palm empty fruit bunches (OPEFB) contains cellulose as its major component which can be isolated and modified into water soluble biopolymers for many applications such as coag-flocculants. Although several efforts have been made in transforming cellulose into quaternized coag-flocculants, the conversion of cellulose isolated from OPB as quaternized coag-flocculants has only so far been carried out by our research group (Mohtar et al. 2016).

The quaternized celluloses were prepared by a varying molar ratio of 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) to anhydroglucose unit (AGU) cellulose and their performance as coag-flocculants were evaluated. It was found that the 9QC prepared using CHPTAC:AGU of 9:1 showed the highest turbidity removal efficiency (ε_t). The performance of the coag-flocculation process is generally effected by independent variables such as coag-flocculant dosage, pH, particle concentration, sedimentation time, and concentration of other pollutants which can be optimized using the response surface methodology (RSM).

The application of RSM is an essential and widely used method to attain optimum experiment values. This statistical approach is able to provide information regarding optimum values related to the proximity of the predicted response in order to get desirable responses, to establish an approximate correlation between dependent and independent variables, and to determine the significance level of the independent variables (Mason et al. 2003; Khuri and Mukhopadhyay 2010). Thus, this study specifically focused on optimizing the independent variables, namely coag-flocculant dosage, pH, and kaolin concentration of the coag-flocculation process using the 9QC carried out using the central composite design (CCD) of the RSM toward obtaining the optimum-dependent variable responses of the ε_t and the sludge volume index (SVI). The optimum values obtained were then used in the coag-flocculation process of the river water using the 9QC with comparison to alum which is commonly used in the drinking water treatment process.

Materials and methods

Materials

The oil palm empty fruit bunch (OPEFB) was obtained from T&H Coconut Fiber Sdn. Bhd. (Johor, Malaysia). The

kaolin powder, isopropanol, ethanol, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), NaOH, acetone, and H_2SO_4 were purchased from Merck (Germany), while 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) was purchased from Sigma-Aldrich (USA). All chemicals used were of analytical grade and used as received. Aluminum sulfate ($Al_2(SO_4)_3{\cdot}14H_2O$) or alum was a gift by the Syarikat Air Johor (SAJ) Sdn. Bhd. (Johor, Malaysia). The double-distilled water produced using the AWS/4D Aquamatic Water Stills Hamilton (UK) was used throughout the experiments.

Methods

Synthesis of 9QC

The cellulose (weight-average molecular weight: 1869 g/mol, polydispersity: 1.465) was isolated from OPEFB by dissolution in [bmim][Cl] at 110 °C for 8 h and then treated with 5 wt%. NaOH solution at 50 °C for 2 h. The modification of the extracted cellulose was carried out by the reaction with CHPTAC in NaOH/urea/thiourea solution (8:8:6.5, w/w) at 9:1 molar ratio (CHPTAC:AGU) and denoted as 9QC.

Coag-flocculation experiments

The coag-flocculation experiment was conducted using a jar test apparatus which consists of batch experiments involving rapid mixing, slow mixing, and sedimentation. The jar test was equipped with six (75 mm × 25 mm) rectangular paddle stirrers (model VELP Scientifica JLT6, Italy) with a capacity of 1 L. Six sets of 1000 mg/L kaolin suspension were prepared by dispersing 0.3 g kaolin powder in 300 mL of double-distilled water. The solutions were adjusted to pH 7 and stirred for 1 min using the apparatus. The initial turbidity of the suspensions was recorded. The coag-flocculation experiments were conducted simultaneously. The solutions were rapidly stirred for 3 min at 250 rpm before slow mixing at 30 rpm for 30 min and then were left for 30 min to allow the sedimentation process. The turbidity of the sample after the coag-flocculation experiment was recorded and the ε_t (%) was calculated according to Eq. (1):

$$\varepsilon_t(\%) = \left(\frac{T_{\text{initial}}(\text{NTU}) - T_{\text{treated}}(\text{NTU})}{T_{\text{initial}}(\text{NTU})}\right) \times 100\,\% \qquad (1)$$

where T_{initial} and T_{treated} are the turbidity of kaolin suspension before and after coag-flocculation process, respectively, in nephelometric turbidity unit (NTU). The SVI (mL/g) determines the settled sludge volume of a kaolin suspension after 30 min of the settlement process, which can be calculated using Eq. (2):

$$\text{SVI}\,(\text{mL/g}) = \frac{\text{settled sludge volume}\ (\text{mL/L}) \times 1000\,(\text{mg/g})}{\text{suspended solids}\ (\text{mg/L})}. \qquad (2)$$

Experimental design and data analysis

An experimental design is necessary to have a sufficient and dependable measurement of the responses of interest. In this study, a second-order model was used to approximate the responses in the region close to the optimum. The CCD was selected as a tool to fit the second-order model. The coag-flocculant dosage (X_1), pH (X_2) and kaolin dosage (X_3) were chosen as three independent variables in the coag-flocculation experiment, and a 2^3 full factorial CCD was made rotatable on the axis at a distance, $\alpha = 1.681$ from the axial point for each factor. The relationships between the coded (x_i) and real (X_i) values of independent variables are given by Eq. (3):

$$x_i = \frac{(X_i - X_0)}{\delta X}, \qquad (3)$$

where X_0 is the value at the center point and the δX is the step change. The different variables have different units and variation limits; as a result, the significance of their effects can be compared after they were transformed into dimensionless-coded values as shown in Table 1.

The optimization of the coag-flocculation variables was analyzed by fitting to a second-order polynomial model using the Statistical 8.0 software. The quadratic equation model for predicting the optimum conditions can be expressed as stated in Eq. (4):

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j, \qquad (4)$$

where Y is the predicted response (i.e., ε_t and SVI), b_0 is the constant coefficient, b_i is the linear coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the interaction coefficient, and x_i, x_j are the coded values of the variables. The sufficiency of the proposed model was determined using the diagnostic checking tests provided by analysis of variance (ANOVA). The quality of the fit polynomial model is expressed by the coefficient of determination (R^2).

Table 1 Experimental ranges and levels of independent variables

Variables	Factor	Range and level				
		$-\alpha$	-1	0	1	α
Coag-flocculant dosage	X_1	0	25	50	75	125
pH	X_2	2	3	7	11	12
Kaolin concentration	X_3	50	500	1000	1500	2000

Coag-flocculation processes of river water

A river water sample was collected from a river located at Skudai, Johor, Malaysia, which was a source for drinking water treatment process. The water sample was collected at least 5 cm below the river water surface and the pH was recorded instaneously. The coag-flocculation experiment was conducted upon arrival to the laboratory and the river water sample was kept in a refrigerator at 4 °C to preserve its conditions. The coag-flocculation processes were carried out at pH 7, thus the water sample was adjusted to pH 7 using 0.01 M HNO_3 solution. A 62.5 mg/L of 9QC was added into the sample and the coag-flocculation experiment was conducted according to the aforementioned procedure, and as comparison, alum was used with the same dosage. Several water quality parameters such as biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solid (TSS), SVI, total solid content, color, turbidity, and heavy metals content were analyzed before and after the coag-flocculation processes.

Results and discussion

Predicted models and validation analysis

The response values obtained from the experiment at various coag-flocculation process conditions are listed in Table 2. Based on the CCD, the following mathematical equations of a final regression model for the responses as a function of coded factors were developed. The results of the fitted model for ε_t are given by Eq. (5) and SVI by Eq. (6):

$$\hat{Y}_1 = 98.84 + 0.22X_1 - 3.65X_2 + 9.87X_3 - 6.56X_1^2 - 4.86X_2^2 - 5.17X_3^2 + 1.54X_1X_2 + 0.88X_1X_3 + 1.15X_2X_3 \quad (5)$$

$$\hat{Y}_2 = 5.67 - 0.74X_1 + 1.12X_2 - 7.92X_3 + 1.54X_1^2 + 1.34X_2^2 + 6.97X_3^2 - 0.82X_1X_2 - 0.31X_1X_3 - 0.15X_2X_3 \quad (6)$$

where X_1, X_2 and X_3 are the coded value of the independent factors (i.e., coag-flocculant dosages, pH, and kaolin concentration). The coefficient with a single factor represents the effect of the specific factor in linear model and the coefficient with two factors represents the interaction between the corresponding factors. Meanwhile, the second-order term corresponds to the quadratic effect of the corresponding factors.

The quadratic models of the Eqs. (5) and (6) were found to be significant at 95 % of confidence level assessed by the Fisher's statistical test (F test) for both responses based on the ANOVA results which are presented in Table 3. The Fisher value (F value) computed by the ε_t and SVI were 68.23 and 113.67, respectively. These values were greater than the F value of 2.137 which was interpolated from the tabulated data in Table VI F-critical points at the 95 % level of significance to reject the null hypothesis (Cornell 1990). In addition, as depicted in Table 3, the calculated probability (p value) for the lack-of-fit of the F test for both responses were <0.05 of significant levels suggesting that the models fit the data well.

A measure of the model's overall performance known as the R^2 and adjusted coefficient of determination (R^2_{adj}) must also be considered in order to check the fit quality of the models. The value of R^2 indicates an agreement between the designated and observed values. However, the R^2 exhibits a systematic error in estimation of values. In this case, R^2_{adj} should be taken into account as this value provides a more accurate goodness-of-fit measurement than the R^2. Additionally, the R^2_{adj} also allows the degrees of freedom associated with sums of square to be considered in the lack-of-fit test. The high value of R^2 (>0.75) for both responses implies a good agreement between the predicted and experimental values (Haaland 1989). Furthermore, if a significant difference between the value of R^2 and R^2_{adj} is found, important and adequate variables have been excluded in the models.

The normal probability plots of residuals are a tool for diagnosing substantive departures from normality. Normally distributed data are presented with an image plot that seems to be a straight line. Any significant deviations from the straight line imply the departures from normality, suggesting that other residuals besides noise are presented in the developed mathematical model. As illustrated in Fig. 1a, b, a fairly straight data plotting is shown for normal probability plot of ε_t and SVI, and a very few deviations from the straight lines were observed for SVI, thus, negligible. This suggested the consistency of the data from a normal distribution and the existed residuals were pure noise. Moreover, the plots of predicted versus experimental values where there was no significant deviation of the values suggest that the overall second-order models as depicted in Eqs. (5) and (6) for the ε_t and SVI, respectively, were significant and adequate.

Optimization of dependent variables

Optimization of turbidity removal efficiency (ε_t)

Table 4 depicts the linear, quadratic, and interaction terms of independent factors for the ε_t. The statistical analysis results show that the linear and quadratic terms of independent factors were significant as indicated by the p value of lower than 0.05. The interaction effect between coag-flocculant dosage and pH was also significant. The p value

Table 2 Full factorial CCD matrix of ε_t and SVI optimization

Run	Independent variables			Dependent variables	
	Coag-flocculant dosage (X_1)	pH (X_2)	[Kaolin] (X_3)	Turbidity removal efficiency (ε_t) (%)	Sludge volume index (SVI) (mL/g)
1	−1	−1	−1	80.33	19.17
2	−1	−1	1	96.02	8.17
3	−1	1	−1	64.12	25.00
4	−1	1	1	86.12	12.17
5	1	−1	−1	75.16	20.83
6	1	−1	1	99.42	7.50
7	1	1	−1	72.37	23.33
8	1	1	1	92.62	9.50
9	−α	0	0	82.33	10.56
10	α	0	0	75.24	7.50
11	0	−α	0	88.33	8.06
12	0	α	0	80.22	9.17
13	0	0	−α	66.24	40.00
14	0	0	α	98.23	8.23
15	0	0	0	99.65	5.83
16	0	0	0	99.24	5.56
17	−1	−1	−1	81.24	20.00
18	−1	−1	1	96.13	8.33
19	−1	1	−1	62.23	25.83
20	−1	1	1	89.22	12.33
21	1	−1	−1	78.26	21.67
22	1	−1	1	99.57	7.50
23	1	1	−1	70.22	23.33
24	1	1	1	95.59	9.33
25	−α	0	0	80.21	11.11
26	α	0	0	77.23	7.78
27	0	−α	0	87.13	8.33
28	0	α	0	77.23	9.44
29	0	0	−α	65.13	43.33
30	0	0	α	96.22	8.37
31	0	0	0	98.23	6.11
32	0	0	0	99.33	5.56
33	−1	−1	−1	79.26	20.83
34	−1	−1	1	94.24	8.33
35	−1	1	−1	66.13	26.67
36	−1	1	1	87.36	12.50
37	1	−1	−1	77.26	22.50
38	1	−1	1	98.72	7.67
39	1	1	−1	69.13	22.50
40	1	1	1	93.46	9.67
41	−α	0	0	81.33	11.11
42	α	0	0	73.27	7.78
43	0	−α	0	86.33	8.06
44	0	α	0	79.12	9.44
45	0	0	−α	70.13	40.00
46	0	0	α	97.23	8.09

Table 2 continued

Run	Independent variables			Dependent variables	
	Coag-flocculant dosage (X_1)	pH (X_2)	[Kaolin] (X_3)	Turbidity removal efficiency (ε_t) (%)	Sludge volume index (SVI) (mL/g)
47	0	0	0	99.12	5.56
48	0	0	0	98.86	6.11

Table 3 ANOVA results of ε_t and SVI optimization

	Sum of square	Degree of freedom (*df*)	Mean square	*F* value	$p > F$
Turbidity removal efficiency [ε_t (%)]					
Regression	6109.93	9	678.88	68.23	<0.0001
Residual	378.09	38	9.950		
Total	6488.02	47			
$R^2 = 0.941$		$R^2_{adj} = 0.928$			
Sludge volume index [SVI (mL/g)]					
Regression	4126.98	9	458.55	113.67	<0.0001
Residual	153.29	38	4.03		
Total	4280.27	47			
$R^2 = 0.964$		$R^2_{adj} = 0.956$			

of the interaction effect between coag-flocculant dosage and kaolin concentration, as well as pH and kaolin concentration was >0.05 indicating that these effects were insignificant. The strongest influence on the corresponding responses is indicated by the highest regression coefficient value as given by Eq. (5). The kaolin concentration and the interaction between coag-flocculant dosage and kaolin concentration showed the strongest and least significant factor for the ε_t, respectively.

The 3D surface and contour plots rendering of the ε_t as a function of the experimental variables are illustrated in Fig. 2. The response surface of the optimum condition of studied variables was precisely inside the design boundary. The corresponding two-dimensional contours show a considerable curvature in contour curves indicating that the three independent factors were interdependent resulting in interactive effects between coag-flocculant dosage and pH, coag-flocculant dosage and kaolin concentration, pH and kaolin concentration on turbidity removal. As shown in Fig. 2a(i), the ε_t increased with coag-flocculant dosage and pH values. As depicted in figure, the ε_t which was higher than 90 % was obtained at pH higher than 4 and coag-flocculant dosage higher than 35 mg/L, respectively. However, as the pH and coag-flocculant dosage value increased and went beyond the optimum region, the removal of turbidity decreased. The same trend was observed in Fig. 2a(ii, iii). The contour plot of the coag-flocculant dosage with respect to kaolin concentration shows that the optimum conditions for the response were located in the region where the coag-flocculant dosage ranging from 35 to 90 mg/L and kaolin concentration ranging from 1100 to 2000 mg/L. Meanwhile, as shown in Fig. 2a(iii), the optimum conditions for pH ranging from 4 to 9 and kaolin concentration ranging from 1100 to 2000 mg/L, respectively. The exact optimum settings to get the maximum ε_t (>99 %) were: coag-flocculant dosage, 60.19 mg/L; pH 6.5; and kaolin concentration, 1557.57 mg/L. Similar results were found by Nourani et al. (2016) who used anionic cotton cellulose as a flocculant in removing positively charged kaolin suspension. The increased dosage and pH to a certain amount increased the removal turbidity to the maximum and then decreased at further increment. A high turbidity removal was found at a high initial kaolin suspension turbidity of 600 NTU (Muyibi and Evison 1995), which was much lower than in the present study (500 NTU–2000 NTU); thus a higher removal is feasible.

It is well known that the major mechanism in a cationic coag-flocculant is a charge neutralization. The existence of different charges induces mutual attraction between particles to spontaneously agglomerate until a repulsion force preventing them to cohere resulted in an increase in the stability of the suspension. In acidic condition, the cationic group of 9QC was protonated which attracts the negatively charged particles. However, a too high protonation due to very low pH can cause charge

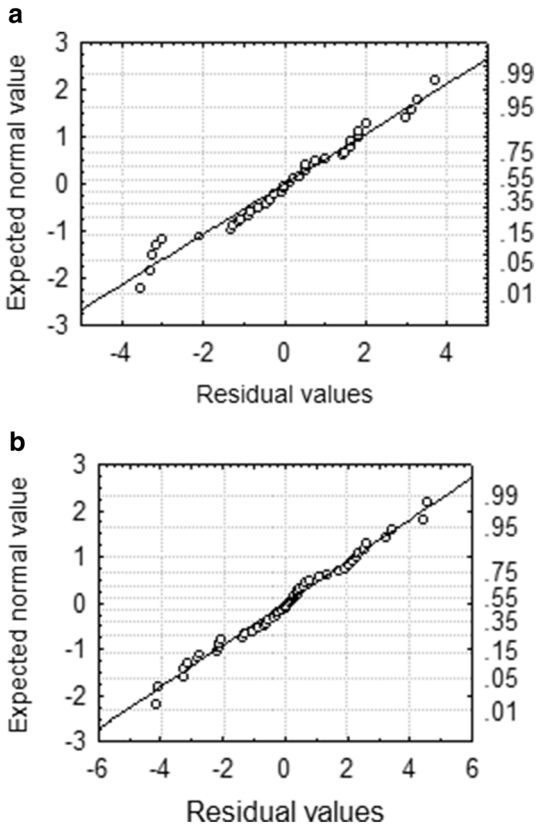

Fig. 1 Normal probability plots of residuals of **a** ε_t and **b** SVI

reversal and increases stability of the particle suspension resulting in low ε_t at low pH. At higher pH, the ε_t value was still higher even though the 9QC was expected to be deprotonated. This is due to the fact that 9QC has a high substitution of cationic moieties on the cellulose backbone (Shi et al. 2012). A similar result was found with the coag-flocculant dosage, in which, a high ε_t could also be obtained if the coag-flocculant dosage was sufficiently added. Insufficient dosing resulted in inadequate cationic charge for the neutralization process causing an ineffective agglomeration of the particles (low ε_t). However, an excess addition of coagulant and flocculant would initiate floc breakup due to charge reversal (Nourani et al. 2016). The high turbidity removal at a high kaolin concentration was due to the increased amount of available suspended particles for adsorption and bridging formation. The effect increased as the particle collision frequency and agglomeration rate increased (LaMer and Healy 1964; Birkner and Morgan 1968).

Optimization of sludge volume index (SVI)

Table 4 shows the linear, quadratic and interaction terms of independent factors for the SVI. It was found that both linear and quadratic terms of independent factors were significant individually based on the p value lower than 0.05. Meanwhile, the interaction terms between the independent variables seems less significant since p value higher than 0.05. The Eq. (6) indicates that the low SVI values obtained in this study seem to be strongly related to kaolin concentration in the linear term. The effects of independent variables can be easily discussed through the quadratic surface response and contour plots of SVI as a function of experimental factors which are illustrated in Fig. 3. The SVI value decreased with the increasing coag-flocculant dosage and pH values as depicted in Fig. 3a. The optimum SVI value was obtained at coag-flocculant dosage higher than 40 mg/L and pH higher than 5. As the coag-flocculant dosage and pH increased beyond the optimum region, the SVI increased, indicating the deterioration of the SVI. A similar trend is found in Fig. 3b. The contour plot of the kaolin concentration as a function of coag-flocculant dosage shows that the optimum conditions for the response were located in the region of 35–110 mg/L for coag-flocculant dosage and 1100–1700 mg/L kaolin concentration. The contour plot of kaolin concentration with respect to pH in Fig. 3c(i) shows that the optimum conditions for the SVI were falling in the region where the kaolin concentration ranging from 1100 to 1600 mg/L and pH ranging from 4 to 8.5. To be precise, the exact optimum experiment conditions to obtain the minimum SVI were: coag-flocculant dosage, 73.53 mg/L; pH 6.7 and kaolin concentration, 1383.3 mg/L.

It was reported that the SVI value was regulated by osmotic pressure, hydration force and polymer effects (Ives and Al Dibouni 1979). The coag-flocculant used in this study possessed a positive charge as opposed to the negatively charged kaolin particles. When two negatively charged kaolin particles approach each other in a suspension, in the presence of coag-flocculants, their counterion atmosphere interfered and screened the double layer repulsion. The interaction between the repulsion and attraction forces created a potential barrier. This barrier can be overcome when enough energy is gained from the random Brownian motion, hence, initiating the coagulation of the particles. Additionally, the gap region between two particle surfaces is decreased, causing the osmotic pressure and hydration force to be reduced, consequently reducing the range of repulsive force and considerably, accumulating the sludge and releasing their bonding water molecules. The increasing amount of kaolin concentration was sufficient with the dosage of coag-flocculant until it reaches the optimum value. The low amount of kaolin concentration might overdose the system with positively charged species, thus, increases the osmotic pressure by incrementation of ionic concentration in the gap region and hydration effect by polarization of nearby water molecules and cause

Table 4 Estimation of the second-order response surface parameters of dependent variables

Parameter	Degree of freedom (*df*)	Effect	Standard error (SE)	*F* value	*p* value
Turbidity removal efficiency [ε_t (%)]					
X_1	1	0.434	0.986	0.1938	0.662237
X_2	1	−7.296	0.986	54.795	0.000000
X_3	1	19.74	0.986	401.231	0.000000
X_1^2	1	−13.118	1.197	120.164	0.000000
X_2^2	1	−9.730	1.197	66.106	0.000000
X_3^2	1	−10.340	1.197	74.662	0.000000
X_1X_2	1	3.087	1.288	5.745	0.021555
X_1X_3	1	1.767	1.288	1.882	0.178136
X_2X_3	1	2.298	1.288	3.185	0.082282
Sludge volume index [SVI (mL/g)]					
X_1	1	−1.481	0.617	12.897	0.000930
X_2	1	2.232	0.617	13.571	0.000713
X_3	1	−15.843	0.617	14.498	0.000498
X_1^2	1	3.081	0.749	29.835	0.000003
X_2^2	1	2.687	0.749	696.300	0.000000
X_3^2	1	13.944	0.749	326.607	0.000000
X_1X_2	1	−1.640	0.806	3.995	0.052827
X_1X_3	1	−0.610	0.806	0.556	0.460681
X_2X_3	1	−0.305	0.806	0.139	0.711482

restabilization. Too high kaolin concentrations, need a higher coag-flocculant dosage for destabilization of colloidal particles to take place.

The effects of pH onto SVI were similar to the pH effects onto the ε_t. As the active sites of the coag-flocculant were protonated at acidic conditions, the osmotic pressure and hydrating effects of the system were also reduced which led to a lower SVI value. However, a too high protonation of the 9QC at very low pH caused a reverse effect resulting in higher SVI. On the other hand, a high pH value increases the osmotic pressure and the hydration force effect, thus, a higher SVI value was obtained.

Optimization of overall dependent variables and validations of the models

The optimization of the two individual responses, namely ε_t and SVI were attained under different optimum conditions. A compromise between the optimum conditions of the two responses is needed as the optimum conditions of each response might impact the other response differently. The desirability function of 99 % and 8 mL/g for ε_t and SVI, respectively, were defined to profile the predicted value and desirability of responses. Figure 4 illustrates the area of feasible overall optimum conditions in the factor space. The effective region of desirability value was smaller than the individual response contour plots due to the overlaid of both responses. The range of coag-flocculant dosages, pH, and kaolin concentration was between 50–70, 5.5–7, and 1200–2300 mg/L, respectively. Specifically, the value of overall response desirability was 62.5, 7.0, and 1400 mg/L for coag-flocculant dosage, pH, and kaolin concentrations, respectively, to obtain >99 % of ε_t and 10.74 mL/g of SVI.

To confirm the agreement between the results achieved from the model and experiment, additional experiments were conducted using the overall optimum experimental settings. The results are shown in Table 5. It was found that both experimental values of ε_t and SVI were close to the predicted values. This indicates that the developed mathematical models as well as the RSM approach were suitable to optimize the coag-flocculation process of 9QC in kaolin suspension. The region for optimum conditions at desired responses was large, indicating that 9QC was effective in a wide range of experimental conditions. This is favored as the 9QC is potentially applicable in a real river water treatment plant which have more complex contaminants, and thus, the study of coag-flocculant effect on the process is of interest.

Coag-flocculation process of drinking water source

The river water sample was analyzed for water quality parameters that influence the performance of the treatment process. The turbidity of river water has become the main problem in water treatment for producing drinking water since it is visibly detected. Table 6 shows the result of river water quality before and after being treated with alum and 9QC. The initial turbidity of the river sample was much

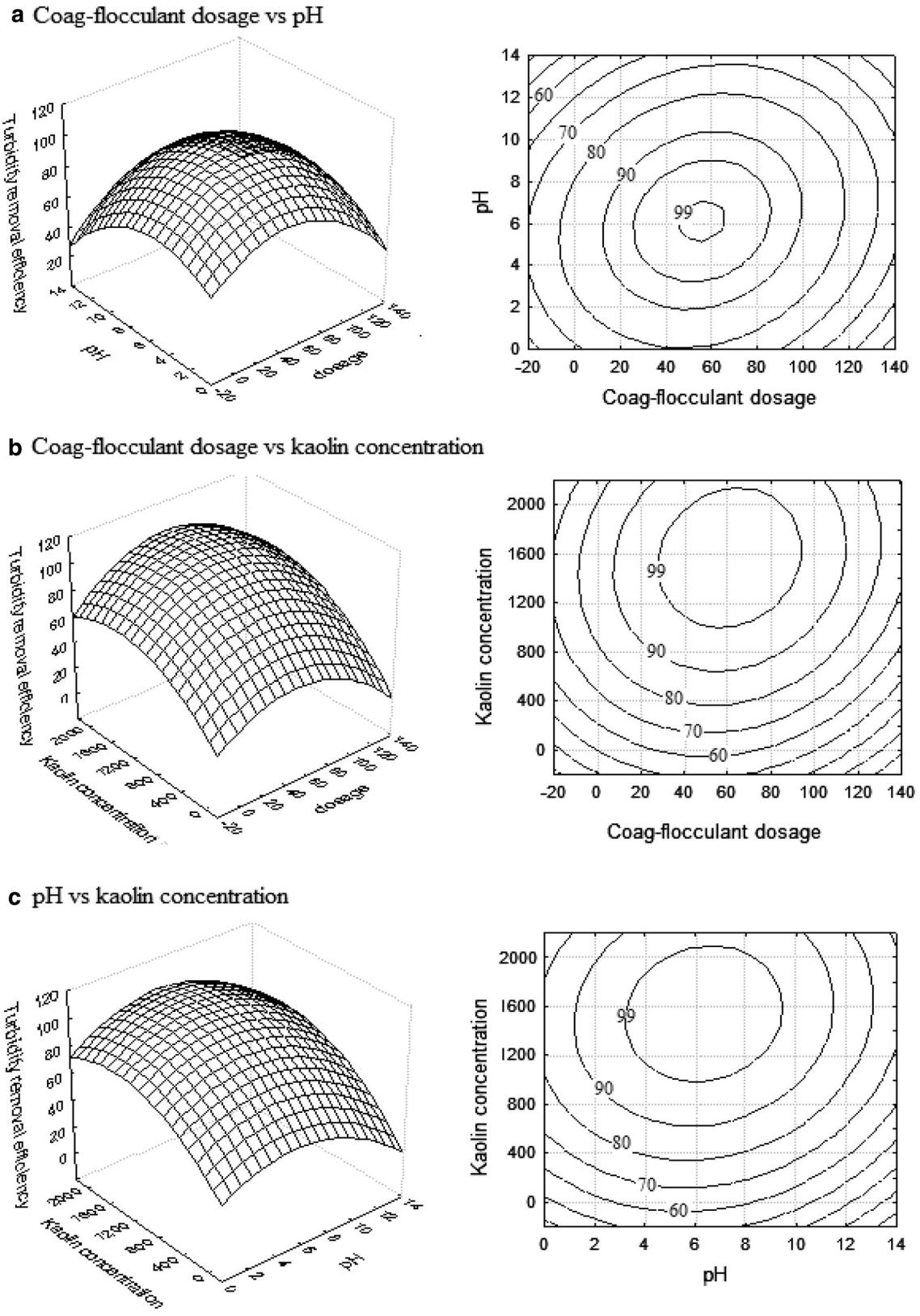

Fig. 2 3D response surface and 2D contour plots of ε_t optimization

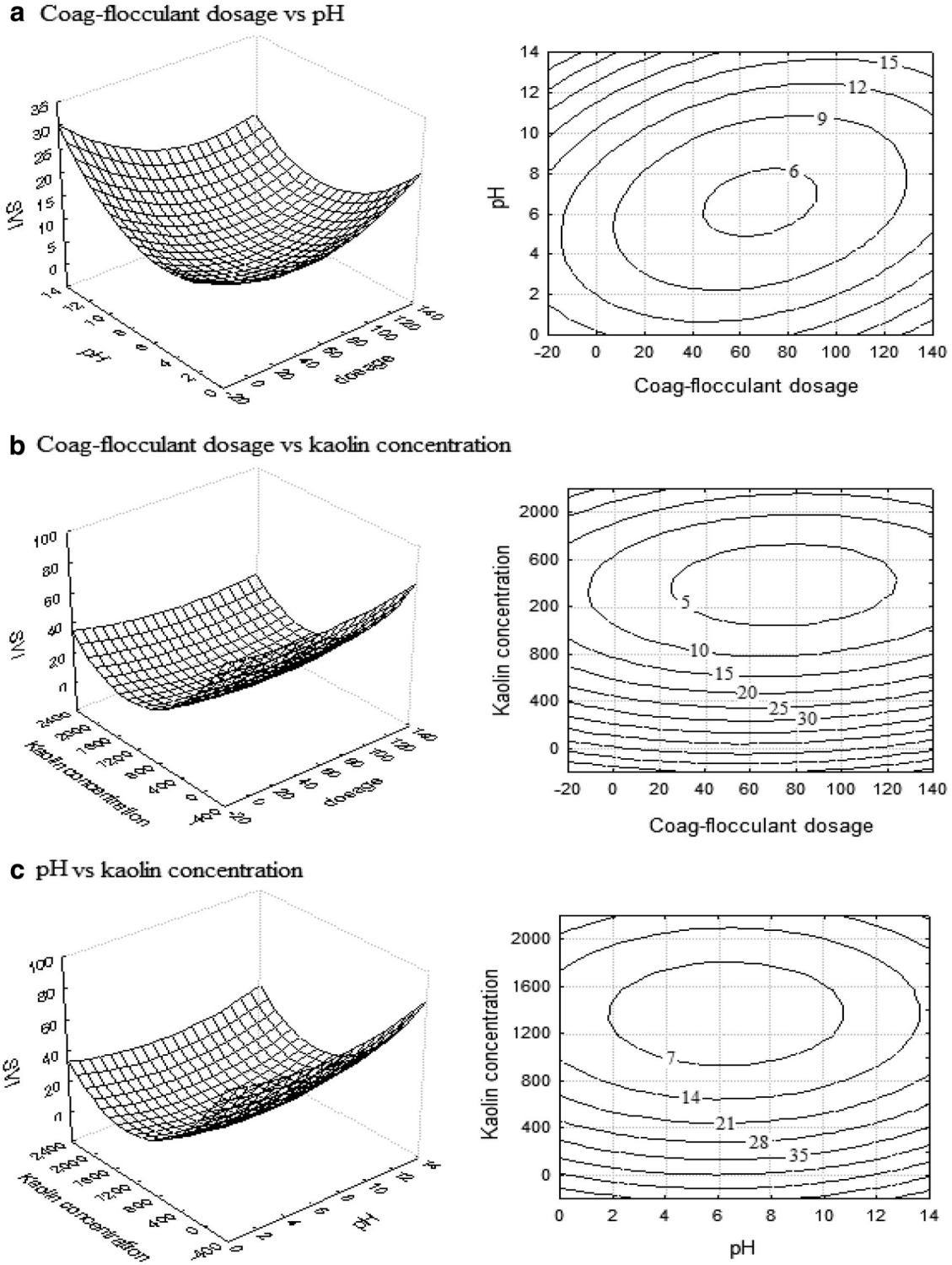

Fig. 3 3D response surface and 2D contour plots of SVI optimization

higher than its standard limit and the turbidity could be observed. After the coag-flocculation processes, the turbidity value decreased to <5 NTU which is required in water quality standard.

An increase in turbidity can often indicate potential in contaminant since pollutants can attach to suspended solids. Turbidity removal determines the removal of suspended solids, thereby other pollutants attached to them. The 9QC

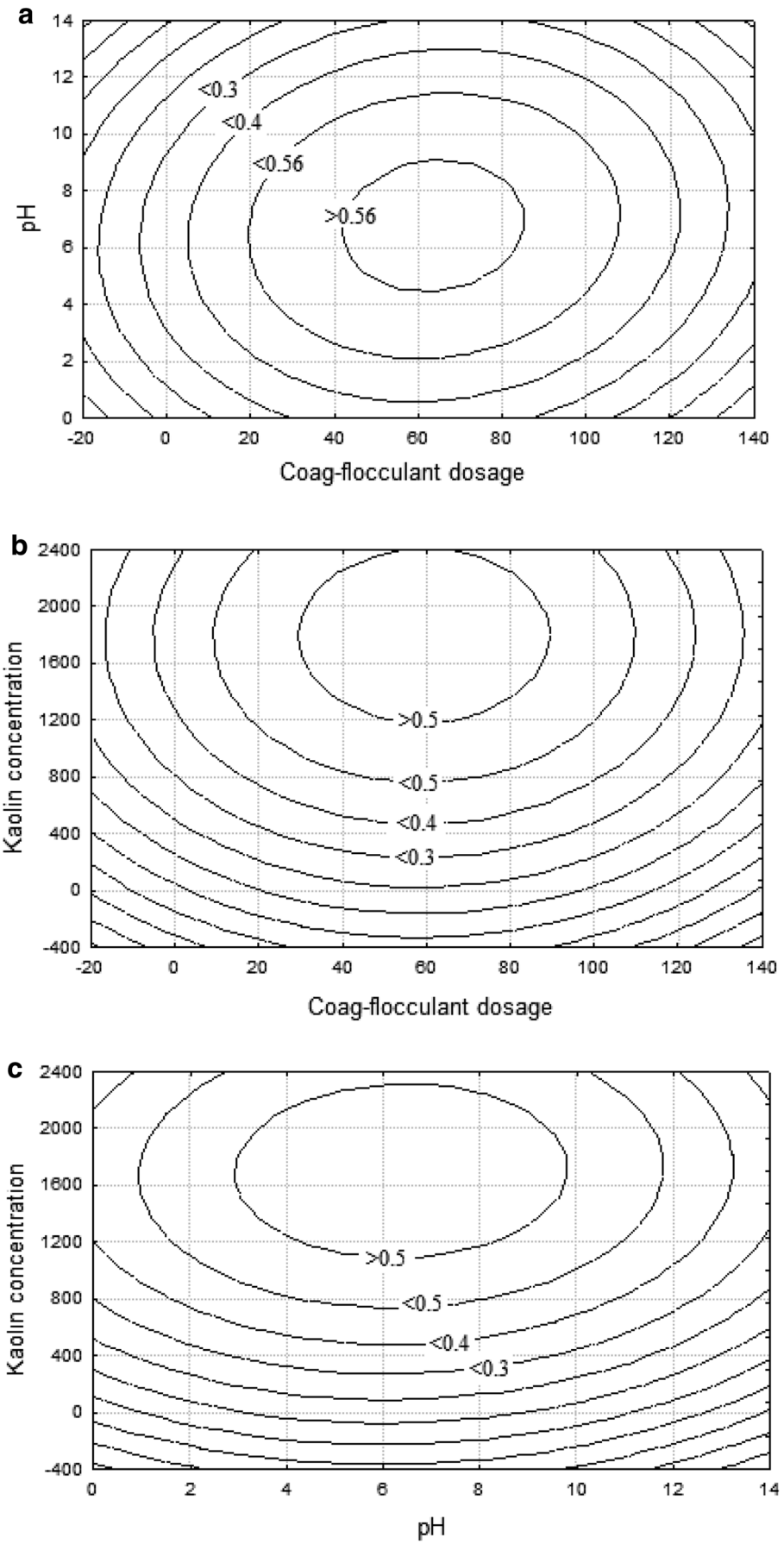

Fig. 4 2D contour plot of overall optimum experimental conditions

Table 5 Validation of overall optimized dependent variables

	Unit	Experimental value	Predicted value
Independent variables			
Coag-flocculant dosage	mg/L	62.50	62.50
pH		7.00	7.00
Kaolin concentration	mg/L	1400.00	1400.00
Dependent variables			
Turbidity removal efficiency (ε_t)	%	99.53 ± 0.08	101.38
Sludge volume index (SVI)	mL/g	9.29 ± 0.50	10.74

Table 6 Characterization of river water before and after coag-flocculation processes

	Sample ID				
	Unit	River water	Alum	9QC	Standard limit[a]
BOD_5	mg/L	5.85	1.55	2.95	30[a]
COD	mg/L	21	32.3	23.3	200[a]
Color	pt-co	82.02	2.12	0.71	15[b]
TSS	mg/L	31	n/a	n/a	30[a]
Total solid	mg/L	340	–	–	–
Turbidity	NTU	44.38	2.53	2.89	5[b]
SVI	mL/g	–	16.13	21.51	–
Heavy metals					
Cd	µg/L	0.011	0.01	0.015	3[b]
Cr	µg/L	2.95	0.81	2.08	50[b]
Cu	µg/L	2.87	0.92	1.11	2000[b]
Fe	µg/L	226.95	29.81	26.41	300[b]
As	µg/L	5.58	1.16	4.43	10[b]
Pb	µg/L	0.206	0.091	0.047	10[b]
Hg	µg/L	11.34	9.59	1.39	6[b]
Zn	µg/L	4.22	2.25	1.29	3000[b]

[a] Sustainable Water Group, Water Quality Guidelines (2010)

[b] Guidelines for Drinking water Quality, WHO (2011)

significantly reduced several contaminants except for the BOD_5 and COD tests (Table 6). The final BOD_5 and COD values were higher than the initial ones, although a high turbidity removal for alum (94.3 %) and 9QC (93.5 %) were obtained. This might be due to the 9QC and alum residues in the water after coag-flocculation process. The initial value of the turbidity (44.38 NTU) was much lower than the concentration of kaolin in suspension used in this study (Table 6). With the low turbidity value, ineffective destabilization of kaolin particles should be expected after the addition of high dosage of the coag-flocculant. However, it should be noted that the contaminants in the river water are much complex than in kaolin suspension as well as much smaller colloidal size causing complication and recalcitrant in separation with the water. Thus, it was necessary to add a higher dosage in order to effectively destabilize the particles for easy removal afterward. Generally, the coag-flocculant can be removed from the water after settling down together with the aggregated colloidal particles. A sufficient coag-flocculant dosage resulted in the absence or low surplus of the coag-flocculant in the sample. A too high dosage resulted in a high coag-flocculant remaining in the sample and might deteriorate the removal efficiency, and a too low dosage resulted in inefficient coag-flocculation process (Wang et al. 2014; Nourani et al. 2016). An optimum dosing might give a better turbidity removal as well as low BOD_5 and COD values.

Besides overdosing, the molecular property of the 9QC might also cause a high coag-flocculant retaining in the sample. The modification of cellulose with CHPTAC not only provided positive charge moieties onto the cellulose backbone, it also increased the hydrophilicity of the natural polymer. This explains the solubility of the highly crystalline material in water. This high hydrophilicity property has caused the 9QC to be hardly separated from water. It is expected that it has also very low hydrophobicity due to its lower molecular chain as compared to the one reported in literature (Sun and Sun 2002). The hydrophobicity property of the natural polymer comes from the polymer backbone. In the meantime, the coag-flocculation process using alum seems to have no effect on the BOD_5 although the COD value was higher than the initial value. This was due to the fact that the alum is an inorganic chemical, while the 9QC is an organic chemical derived from a biomaterial which can be easily degraded; thus it resulted in a higher BOD value after 5 days.

It is generally known that turbidity is not the only problem in the river water pollution. Other contaminants such as heavy metals, namely mercury (Hg), cadmium (Cd), chromium (Cr), and lead (Pb) which are known to be highly toxic were also found in the river water (Sanz-Medel 1998; Xiong and Yao 2009). The existence of these metals in surface water is predominantly associated with suspended particles. A very small amount of heavy metals is traced as dissolved matters (Kennish 1997). Therefore, the high removal of heavy metals depends on the efficient removal of suspended particles in the river water. Table 6 shows that most of the heavy metals in the samples were lower than the standard limit except for Hg. The Ferum (Fe) content in the river water also caused concern as the

content nearly reached the standard water quality limit. Both alum and 9QC were proven to be able to remove heavy metals by a certain degree. For example, the alum could remove Cd better than the 9QC, but the 9QC could remove zinc (Zn) better than the alum. In the case of Fe and Hg, the 9QC has shown a higher removal than alum, reaching close to the limitation of water quality standards, even though the remaining turbidity was higher as compared to alum. As polysaccharides, the 9QC has an excellent selectivity toward heavy metal ions due to the existence of active functional groups in the cellulose backbone and has a high capacity to interact physically and chemically with a wide variety of molecules (Abdel-Halim and Al-Deyab 2011). The Hg especially is one of the most toxic heavy metals in aqueous solution, and the removal of these heavy metals is compulsory since it was highly detected in the Sg. Skudai. It was recommended that further research should be done in order to find the optimum value for removal of the contaminants in the river water and covering not only the suspended solids, but also all water quality standards as required and regulated by the local government. The optimum value obtained from the optimization experiment can give an insight on narrowing the coag-flocculant dosage range for further study.

Conclusions

Optimization of independent variables (i.e., coag-flocculant dosage, pH, and kaolin concentration) on dependent variables (i.e., turbidity removal efficiency, ε_t, and sludge volume index, SVI) were successfully carried out using the central composite design (CCD) of the surface response methodology (RSM). The quaternized cellulose from OPEFB (i.e., 9QC) was used as a coag-flocculant in this optimization study. It was found that the optimum conditions for the maximum ε_t (>99 %) was 60.19 mg/L 9QC dosage, pH of 6.5, and 1557.57 mg/L kaolin concentration. The lowest SVI (10.74 mL/g) can be obtained using 62.5 mg/L of 9QC at initial pH value being 7.0 and kaolin concentrations of 1400 mg/L. The overlapping of the optimum region for both responses of interest resulted in the overall optimum values of 62.5 mg/L 9QC dosage, initial pH 7, and 1400 mg/L kaolin concentration. The kaolin concentration resulted as the most influenced variable that gave the highest ε_t and the lowest SVI. The coag-flocculation studies on river water using 62.5 mg/L 9QC at pH 7 have shown encouraging results for most of the water quality tests and heavy metals removal. It can be concluded that the use of 9QC as a coag-flocculant is feasible for drinking water treatment.

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