Production of a biodegradable flocculant from cotton and evaluation of its performance in coagulation-flocculation of kaolin clay suspension: Optimization through response surface methodology (RSM)

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Abstract

Flocculants are widely used along with coagulant to increase the efficiency of coagulation-flocculation process for removal of colloidal particles from wastewaters. The most widely used flocculants are synthetic which have some problems such as non-biodegradability and release of toxic residual monomers. The main aim of this study is to evaluate the performance of cellulose sulfate (CS), which was synthesized through sulfonation of cotton, as a biodegradable and natural-based flocculant. Reaction time as an important factor in the sulfonation reaction was optimized for obtaining CS with high charge density and suitable fiber size. The sulfate content, charge density (CD) and morphology of each CS were determined to investigate and select the best CS for the flocculation process. A suspension containing kaolin clay was used as a colloidal test solution and coagulation was performed using alum (as a coagulant) and CS (as a flocculant). Optimization was performed using response surface methodology (RSM). The optimization results showed that CS had a good performance in turbidity reduction in coagulation-flocculation treatment and maximum turbidity reduction (98.9 %) was obtained at alum dosage of 23.1 mg/L, CS dosage of 7.2 mg/L and pH = 6.2. The results showed that the pH variation had insignificant effect on the CS dosage. Zeta potential measurements and microscopic photos of flocs confirm charge neutralization and bridge formation in flocculation using cellulose sulfate, respectively. Also, the total chemical consumption reduced compared with the use of alum alone. As a consequence, CS can be considered as a suitable alternative for conventional flocculants.

Keywords: Biodegradable; Flocculant; Turbidity removal; Cellulose sulfate; Coagulation-flocculation; Response Surface Methodology

1. Introduction

Coagulation–flocculation treatment is a suitable method for removing colloidal particles from municipal and industrial wastewater. Colloidal particles can be settled and removed easily by neutralization and making them closer. Recently, many studies have been conducted about using the coagulation–flocculation in industries, e.g., dairy [1], pulp [2], drinking water treatment [3], municipal wastewater treatment and pretreatment of landfill leachate [4].

In line with some studies, inorganic coagulants (mainly salts of multivalent metals) such as aluminum sulfate (alum) and ferric chloride have been used without assistance of flocculants [5-7]. Metal salts will hydrolyze rapidly in aqueous medium to form cationic species, and then they will be adsorbed by negatively charged colloidal particles. Therefore, simultaneous surface charge reduction and formation of micro-flocs will happen [3]. The micro-flocs are small and have low strength; therefore they will break down when subjected to physical forces. The low efficiency of the process and presence of metal residue in the supernatant indicate the necessity of using flocculants in coagulation-flocculation treatment [8].

There are a multitude of organic flocculants which most of them are synthetic, including poly-acrylamides, poly-acrylic acids, polystyrene sulfonic acids, and their derivatives. These flocculants are mostly linear water-soluble polymers with repeating units of various monomers, high molecular weight and can be ionic (addressed as polyelectrolyte) or non-ionic.

These flocculants have some problems such as non-biodegradability and release of residual monomers in water, which have adverse effects on the health [9, 10]. So, using of the eco-friendly flocculants as alternative materials for conventional flocculants in water and wastewater treatment is increasing [11, 12].

Cellulose which is the most abundant and the most significant natural polymeric compound, has greatly influenced the human's life [13]. Because of biodegradability, availability, not-toxicity, high purity and low cost [14] it has been mostly considered in the water treatment process during recent years for instance in removal of dyes [15] and heavy metals [16, 17]. Recently, researchers have investigated the application of cellulose-based materials as a biodegradable flocculants in flocculation-coagulation process [3, 18-20]. The desired functionality can be introduced into the cellulose structure in order to prepare the most effective flocculant. Cellulose typically has a very large external surface area covered with hydroxyl groups (2-3 mmol/g). These unique properties provide an ideal platform for surface modification to develop a material with desired surface characteristics customized for a wide range of applications [21]. The flocs of iron hydroxide, which are formed during coagulation process, have positive charge. Therefore an anionic flocculant can interact with positively charged flocs to promote the formation of larger and more shear-resistant flocs as a consequence of bridge formation between destabilized particles. In this paper, cellulose was functionalized through sulfonation reaction to produce cellulose sulfate as an anionic flocculant.

Many factors are effective on the performance of the coagulation-flocculation process, such as dose of coagulant, dose of flocculant and initial pH. In many studies on the coagulation-flocculation for turbidity removal, optimization was usually done by varying one factor while all other factors are constant [3, 18]. This approach, consumes more time and energy and leads to inaccurate optimum because of ignoring the interaction of factors [22]. To overcome these problems, the response surface methodology (RSM) can be considered as an appropriate approach since including the impacts of individual factors and the ones of their interaction. RSM is consist of statistical and mathematical techniques and gives a comprehension of mathematical

correlation between effective factors [4]. Using RSM leads to determine the optimum operational condition and a domain that satisfies the operating properties [23]. Recently, RSM methodology has been used to optimize coagulation-flocculation process for the wastewater treatment [2, 24].

The aim of this research is to study the ability and effectiveness of partially soluble anionic cellulose sulfate (CS) as a novel flocculant for removal of turbidity from aqueous medium containing suspended kaolin clay particles as a source of turbidity. For this purpose, four types of CS with different degrees of sulfonation, particle size and charge density were synthesized. The influences of alum, CS and solution pH on the coagulation-flocculation were studied by determining the residual turbidity of the settled suspension.

2. Materials and methods

2.1. Materials

The cellulose source for this study was hydrophilic natural cotton provided by Panberiz, Iran, company. Chlorosulfonic acid (CSA) and Dimethylformamide (DMF) were supplied by Merck (Darmstadt, Germany) and were used without further purification. Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was employed as an inorganic coagulant agent and was also obtained from Merck. Commercial grade Kaolin clay (Superfine size of 11 μm) was procured from Kanipazhouh, Iran as a dry powder and its water slurry (pH 7.4) was prepared in deionized water without any dispersing agent. The chemical composition of the kaolin sample was found to be SiO_2 60.17%, Al_2O_3 30.10%, Fe_2O_3 0.21%, MgO 0.02%, CaO 0.01%, K_2O 0.13%, TiO_2 0.03%, with LOI of 6.31%. The pH of the kaolin suspension was adjusted using NaOH and HCl purchased from Merck.

2.2. Synthesis of the cellulose sulfate (CS) flocculant

Anionic CS with variable fiber size and charge density was synthesized by hydrolysis and sulfonation of cellulose with CSA in DMF. For this purpose, 3 g of hydrophilic natural cotton was immersed in 45ml of DMF in a dry and clean beaker for 15 minutes at ambient temperature. Then, 4.5 ml of CSA was slowly added to 45ml of DMF in an ice bath. This process was followed by gradually adding this mixture to cotton immersed in DMF. Final mixture in the sealed glass container was shaken at a constant speed of 120 rpm at ambient temperature. Sampling was performed at 45, 60, 75 and 90 min. In order to separate DMF to reuse it, vacuum filtration was utilized. After filtration through a 1- μ m membrane and washing with deionized water, the pH of obtained CS was neutralized by an adequate amount of sodium bicarbonate solution and then was filtered and washed again several times with deionized water. Schematic reaction for sulfonation of cellulose is shown in Fig. 1.

Fig. 1. Sulfonation of cellulose

2.3. Characterization of CS flocculant

Fourier transform infrared (FTIR) spectra of the cotton and CS were recorded using a Bruker FT-IR spectrometer. The amount of anionic groups of the CS was indirectly calculated from the sulfur content of the products, which was determined with an elemental analyzer (Thermo Finnigan, FlashEA 1112 series). Morphological studies of CSs were conducted by scanning electron microscope (SEM, model: HITACHI S-4160). The Malvern Zetasizer 3000

was used to measure zeta potential of the kaolin clay suspension before and after adding alum. A six-beaker jar-test apparatus (Zag-Chemi, Iran) was applied to perform coagulation-flocculation experiments. Residual turbidity of the supernatant was determined by HACH turbidimeter (model 2100Q01).

2.4. Coagulation–flocculation experiments

A standard jar-test was used to simulate coagulation-flocculation process and evaluate the flocculation performance of the CS. Kaolin suspension with a solid content of 5 g/L was used as artificial turbidity. To perform experiments, pH of kaolin clay suspension (400 ml) was adjusted using solutions of 0.1 mol/L HCl and 0.1 mol/L NaOH. The coagulation-flocculation process consisting of rapid mixing (3 min, 180 rpm), followed by slow mixing (15 min, 40 rpm) and settling at room temperature (30 min).

2.5. Experimental design and data analysis

The central composite design (CCD), which is one of the important designs of RSM, was selected for the optimization of the parameters. Since different variables are usually expressed in different units and/or have different limits of variation, the importance of their effects on the response can only be compared after they are coded. A total of 20 experiments according to a 2^3 full factorial CCD, consisting of eight factorial points (coded to the usual ± 1 notation), six axial points ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0), (0, 0, $\pm\alpha$), and six replicates at the center points (0, 0, 0) were conducted. The value of α for rotatability depends on the number of points in the factorial portion of the design, which is given in Eq. (1):

$$\alpha = (N_F)^{1/4} \quad (1)$$

where N_F is the number of points in the cube portion of the design ($N_F = 2^k$, k is the number of factors). Therefore, α is equal to $(2^3)^{1/4} = 1.682$ according to Eq. (1). The relationship between

the coded (x_i) and actual (X_i) values of factors and the ranges of levels are given in Table 1, in which the range of factors is expressed by the values of $X_{\min}$ (minimum value of X) and $X_{\max}$ (maximum value of X).

Table 1 Relationship between the coded and actual values of factors and the levels of the variables tested in the central composite design.

Code (x_i)	Actual value of factor (X_i)	Coagulant dosage (mg/L) (X_1)	Flocculant dosage (mg/L) (X_2)	Initial pH (X_3)
$-\alpha$	$X_{\min}$	5.00	5.00	4.00
-1	$(\alpha - 1)X_{\max} + (\alpha + 1)X_{\min}$	12.09	7.02	4.60
0	$\frac{X_{\max} + X_{\min}}{2}$	22.50	10.00	5.50
1	$(\alpha - 1)X_{\min} + (\alpha + 1)X_{\max}$	32.91	12.97	6.39
$+\alpha$	$X_{\max}$	40.00	15.00	7.00

Turbidity reduction was selected as the dependent variable. The response variable was fitted by a second-order model in the form of quadratic polynomial equation:

$$Y_m = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i=1}^{i < j} \sum_j b_{ij} X_i X_j \quad (2)$$

Where Y is the predicted response (turbidity removal efficiency), b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficient and x_i, x_j are the coded values of the variables. The actual and predicted values are presented in Table 2. The Design-Expert 9 software was used to design experiments and evaluate results.

Table 2. Central composite design matrix with actual and predicted values

Run	Coded values			Turbidity removal (%)	
	Coagulant dosage (X_1)	Flocculant dosage (X_2)	pH (X_3)	Actual	Predicted
1	1.68	0	0	97.42	97.12
2	0	0	0	98.64	98.78
3	-1	1	1	96.42	96.41
4	0	0	0	98.42	98.34
5	0	1.68	0	97.78	97.78
6	1	1	1	98.21	98.14
7	-1.68	0	0	93.71	93.83
8	0	0	0	98.64	98.74
9	0	-1.68	0	97.71	98.01
10	0	0	0	98.42	98.53
11	0	0	0	98.42	98.33
12	-1	-1	-1	94.57	94.04
13	0	0	1.68	98.07	98.21
14	0	0	0	98.64	98.98
15	1	-1	-1	96.21	96.01
16	1	1	-1	96.14	96.10
17	0	0	-1.68	94.07	93.81
18	1	-1	1	98.42	98.33
19	-1	-1	1	96.57	96.92
20	-1	1	-1	94.00	93.03

3. Results and discussion

3.1. Characteristics of CS

FTIR spectra of source of cellulose (cotton) and CS are shown in Fig. 2. Sulfonation of cellulose was confirmed by the appearance of new IR bands at 997 and 1230 cm^{-1} which was respectively assigned to the symmetric and asymmetric stretching vibrations of sulfate group.

Fig. 2. FTIR spectra of (a) cellulose, (b) CS.

The sulfate content of anionic cellulose, which is representative the amount of anionic groups (charge density), was determined using an elemental analyzer. The effect of reaction time on the charge density is shown in Table 3. As can be seen, the charge density increased by increasing the time of reaction.

Table 3. The effect of reaction time on the sulfur content and charge density

Sample	Reaction time	Sulfur (%)	Charge density
CS I	45	9.09	2.84
CS II	60	10.72	3.35
CS III	75	12.77	3.99
CS IV	90	13.57	4.24

SEM images of cotton and CSs were investigated for understanding the surface morphology and fiber structure of synthesized CS. As demonstrated in Fig. 3, the sulfonation of cotton fibers led to significant change in surface morphology, which could be due to hydrolysis and destruction of cellulosic fiber structure in acidic medium. The raw cotton had long, separate and rigid fibers, while by increasing the time of sulfonation, the surface of CSs became smoother. So that, after 60 minutes of sulfonation process, cotton fibers convert to smooth sheets. Our SEM images of CSs are similar to the results of sulfonated cellulose of hardwood kraft pulp, which was obtained by the sulfonation reaction with sodium bisulfite [25].

Fig. 3. SEM images of (a) cotton, (b) CS I, (c) CS II, (d) CS III, (e) CS IV

3.2. Comparison among flocculation efficiency of CSs

In order to select the best CS as the flocculant, several jar tests were firstly performed without flocculent (CS) to choose an appropriate alum dosage at which the surface charge of kaolin clay has to be neutralized and aluminum hydroxide flocs does not have to be formed. As can be seen in Fig. 4, the turbidity of kaolin clay suspension (5 g/L) decreased sharply after adding 20 mg/L alum and this decrease continues up to 250 mg/L. These results indicate that the surface charge of kaolin clay has been neutralized at low dosage of alum by the hydrolyzed cationic aluminum species. In addition, the best coagulation performance of alum has been observed in the pH range of 4.5-6.5 [18]. Hence, the alum dosage of 20 mg/L and the pH of 5.5 were chosen for subsequent tests with CSs to make an appropriate comparison between their flocculation efficiency and sedimentation velocity.

Fig. 4. Effect of alum dosage on the turbidity reduction of a kaolin suspension (5 g/L).
pH: 5.5 , Settling time: 30 min.

Several jar tests were performed to make an appropriate comparison between CSs flocculation efficiency and sedimentation velocity. The results of jar tests are presented in Fig. 5

As it is shown, turbidity reduction and sedimentation velocity is higher for coagulation-flocculation treatment with CS III. It is generally known that the most effective polymers for bridging are those possessing a high molecular weight [26], but the charge density can also have a considerable influence on bridging performance [27]. By increasing the time of reaction, from Cs I to CS IV, the charge density increases, but the fiber size decreases due to hydrolysis and destruction of cellulose fiber structure. The charge density of CS IV is greater than CS III, but its fiber length is smaller, therefore CS III shows better performance in turbidity reduction. Consequently, CS III was chosen for subsequent experiments.

Fig. 5. Comparison among flocculation efficiency of CSs in coagulation-flocculation of kaolin suspension (5 g/L). The alum dosage: 20 mg/L, the CSs dosage: 10 mg/L and pH: 5.5.

3.3. Modeling and statistical Analysis

The second-order polynomial equation was developed to correlate the turbidity removal percentage (Y) as the function of coagulant dosage (X_1), flocculant dosage (X_2) and pH (X_3).

The following equation is a regression model with the experimental results:

$$Y = 53.5305 + 0.4358X_1 + 0.2068X_2 + 12.4641X_3 + 0.0048X_1X_2 + 0.0083X_1X_3 + 0.0495X_2X_3 - 0.0095X_1^2 - 0.0295X_2^2 - 1.0743X_3^2 \quad (3)$$

Statistical testing of the model was performed with the Fisher's statistical test for analysis of variance (ANOVA). The results of the ANOVA for turbidity reduction are shown in Table 4.

Table 4. Analysis of variance for turbidity removal

Source	Sum of squares	dF	Mean square	F-value	P-value, Prob >F
Model	54.71	9	6.08	444.80	< 0.0001
X ₁	12.50	1	12.50	914.64	< 0.0001
X ₂	7.74×10 ⁻⁴	1	7.74×10 ⁻⁴	0.057	0.8172
X ₃	15.74	1	15.74	1152.05	< 0.0001
X ₁ X ₂	0.13	1	0.13	9.47	0.0132
X ₁ X ₃	0.035	1	0.035	2.58	0.0240
X ₂ X ₃	0.10	1	0.10	7.34	0.1428
X ₁ ²	14.88	1	14.88	1088.85	< 0.0001
X ₂ ²	0.95	1	0.95	69.83	< 0.0001
X ₃ ²	10.22	1	10.22	747.60	< 0.0001
Residual	0.12	9	0.014		
Lack of Fit	0.054	4	0.014	0.98	0.4928
Pure Error	0.069	5			

$$R^2 = 0.9955, \text{Adj } R^2 = 0.9872$$

P-value determines whether *F* value is large enough to indicate statistical significance or not [28]. The *p*-values less than 0.05 indicate that the quadratic model terms are significant.

The model is highly significant with a very low probability value ($P < 0.0001$). On the other hand, the lack of fit for this model (*p*-value=0.4928) is not significant. A R^2 value greater than 0.75 indicate the aptness of the model [29]. As can be seen, R^2 value is high ($R^2 = 0.9955$) and reasonably agreed with the adjusted R^2 value of 0.9872. It means that the quadratic model fits the data and satisfactorily describe the system behavior within the range of operating factors [30]. The observed and predicted values by the quadratic model are shown in Table 2. The agreement between the turbidity removal by the model and the experimental data is very good. Adequate precision ratio obtained were greater than 4, indicating that adequate signal for model could be used to navigate the design space. The obtained ratio of 18.8 indicates an adequate signal.

3.4. Three-dimension response surface and contour plots

For a better explanation of the independent variables and their interactive effects on the turbidity reduction of kaolin clay suspension, 3D plots and its corresponding contour plots are represented in Fig. 6. To detect the interaction between factors, the shape of the contours can be used; indeed an elliptical shape in the contours shows significant interaction between factors, so, by using the response surface plot and the contour of each pair of independent factors, the optimal value of them and their interaction can be understood easily. The central ellipse in the contour diagram represents the highest predicted value for the response in the selected intervals of factors. In fact, elliptical pattern represents some deep interaction between the independent variables.

Fig. 6(a) shows that by increasing the alum and CS to a certain amount, turbidity removal reaches to a maximum and then decreases. This behavior suggests that floc breakup occurs because of charge reversal and dispersion when there is an extreme dosage of coagulant and flocculant [31, 32]. Zeta potential of kaolin suspension before and after adding alum was determined. The results showed that by increasing the alum dosage, the zeta potential decreased from -15.5 ± 2 to -1.2 ± 0.5 mV and after that a charge reversal was observed ($+3.5 \pm 1.2$ mV) as a result of adsorption of excess Fe^{3+} on the surface of particles.

It can be seen in Fig. 6(a) that the turbidity reduction is more dependent on the coagulant dosage. This behavior suggests when the coagulant dosage is not sufficient, colloidal particles neutralization will not occur. Therefore, increasing or decreasing the flocculant dosage (CS) has no influence on the turbidity reduction. The p -value greater than 0.05 for flocculant dosage is also confirmed by the fact that while the surface charge of colloidal particles is not natural, CS dosage has insignificant effect on the turbidity removal.

Fig. 6(b) show that the turbidity removal decreases in the pH lower than 4.5, because the isoelectric point (IEP) of kaolin clay is in the range of 4-5 [32] and at the pH lower than IEP, kaolin clay has positive surface charge. In addition, alum is a cationic coagulant and has no electrostatic interaction with kaolin clay that has positive surface charge. Also, in the pH above 6.5, the turbidity removal decreases because anionic aluminum complexes are formed which can prevent floc formation [2].

The contour plot in Fig. 6 (c) is nearly linear and the p value of X_2X_3 is 0.1428 (p value > 0.05), therefore the interaction between CS dosage and pH is insignificant. The sodium salt of cellulose sulfate is not classified as an acidic or basic flocculant; therefore it is anionic in the wide range of pH and variation of pH has no effect on its charge density, indicating insignificant

interaction between pH and CS dosage. But the charge density of weak acidic flocculants such as carboxymethyl cellulose depends on the pH and it significantly decreases by decreasing the pH. As a consequence, the low dosage of flocculant is required in the higher pH, indicating significant interaction between pH and flocculant dosage.

Fig 6. Surface plots and its corresponding contour plots of turbidity removal showing the effect of variables. (a) Alum dosage-CS dosage at pH of 5.5 (b) Alum dosage-pH at CS dosage of 10 mg/L (c) pH-CS dosage at alum dosage of 22.5 mg/L.

3.5. Mechanism of flocculation with CS flocculant

Kaolin particles are negatively charged in the neutral pH range (pH 6 to 8), causing their particles to remain in suspension without aggregating for long periods of time. Charge neutralization through adsorption of oppositely charged ions can be exploited to destabilize the colloidal suspensions. In order to investigate the neutralization of surface charge of kaolin particles with hydrolyzed cations of alum, zeta potential of suspension before and after adding alum was determined which the results showed reduction in zeta potential from -15.5 ± 2 to -1.2 ± 0.5 mV, respectively. After destabilization of kaolin particles, the cellulose sulfate was added to promote the formation of larger and more shear-resistant flocs as a consequence of bridge formation between destabilized particles. The microscopic photos of flocs in the absence and presence of CS are presented in Fig. 7. The larger flocs obtained in presence of CS confirms the bridge formation performance of cellulose sulfate. In addition to charge neutralization, sweep coagulation has an important role in turbidity reduction [33] through capture of small particles by large flocs in slow mixing.

Fig. 7. Microscopic photos of flocs (a) in the absence of Cs and (b) in the presence of CS (Magnification: 10x)

4. Conclusion

A combined coagulation-flocculation treatment based on alum and a novel, partial soluble anionic cellulosic flocculant derived from cotton, CS, was found to be effective in removal of colloidal particles, as demonstrated using kaolin suspensions. A 2^3 full factorial central composite design and response surface methodology was applied to overcome the limitations of classical methods and was successfully employed to obtain the optimum process conditions while the interactions between process variables were demonstrated. The optimized levels of alum dosage, CS dosage and pH for maximum turbidity reduction (98.9%) were 23.1 mg/L, 7.2 mg/L, 6.2, respectively. In addition, the results revealed that the pH variation had a minor effect on the CS dosage. Formation of larger flocs by bridging mechanism in the presence of CS and sweep coagulation during sedimentation can lead to capture further microflocs. The combined treatment resulted in a lower residual turbidity of settled suspension with remarkably reduced total chemical consumption relative to coagulation with alum alone.

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