Original Research

Wastewater Flocculation Using a New Hybrid Copolymer: Modeling and Optimization by Response Surface Methodology

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Abstract

A new hybrid inorganic-organic copolymer, aluminum chloride-poly(acrylamide-co-acrylic acid), was prepared using the free radical polymerization method and employed in this study. The hybrid copolymer was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy-dispersive x-ray spectroscopy (EDS). This hybrid copolymer was used in the flocculation of wastewater as a new flocculant. The design variables in the flocculation experiments were hybrid copolymer dosage and wastewater pH. The central composite design (CCD) for the response surface methodology (RSM) approach was used to develop a mathematical model and to optimize the parameters of the flocculation process in terms of optimal removal of chemical oxygen demand (COD), total suspended solids (TSS), and turbidity. After applying the analysis of variance (ANOVA) of all quadratic models, it was found that the obtained value of the correlation coefficient (R^2) was more than 0.98 for all models. The optimum hybrid copolymer dosage was 125 mg/l and the optimum pH 7.55. Under these optimum values, the wastewater treatment achieved 97%, 98.6%, and 88.6% removal of turbidity, TSS, and COD, respectively.

Keywords: hybrid copolymer, flocculation, response surface methodology, wastewater treatment

Introduction

Municipal wastewater contains large amounts of pollutants that cause water pollution. Untreated sewage severely pollutes different types of water resources [1]. Therefore, it is necessary to reduce the pollutant concentration in wastewater before discharging it to the environment. Coagulation/flocculation is one of the chemical processes often used in water and wastewater treatment units [2, 3]. This traditional chemical process is use for destabilization of colloidal suspensions and to remove suspended solids and organic matters [4].

The most widely inorganic coagulants used in the coagulation process are aluminum chloride, ferrous sulfate, and aluminum sulfate. In general, the mode of action of these inorganic coagulants can be expressed in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products, and incorporation of impurities by the amorphous hydroxide precipitate [5]. These inorganic coagulants are well-known for their effectiveness, availability, and low cost [6].

Recently, new reagents have been introduced into the coagulation treatment process, and these reagents are cited as inorganic polymeric coagulants. They are more effective than the conventional inorganic as a result of their complex preparation procedures that make them perform better. Lately, prehydrolyzed aluminum coagulants such as polyaluminium silicate chloride (PASiC) has been prepared and applied [7]. Hence, coagulants/flocculants can mainly be classified into three groups [8, 9]:

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(a) inorganic coagulants such as polyaluminum chloride (PAC) and aluminum sulfate (alum)
(b) organic synthetic polymer, such as polyacrylate-based composite polymers
(c) naturally-occurring flocculants, such as sodium alginate, chitosan, starches, and guar gum.

The polymerization of acrylamide can easily be acquired by a free radical polymerization method. The using of synthetic polyacrylates in water treatment facilities produces a sludge with small volume, better dewatering characteristics, and more proper treatment performance. They may also be used as a primary coagulant for the same purpose [10].

When the inorganic salts are added to the organic flocculants, the aggregation power of the flocculants is enhanced by increasing the effective components and then positively charging the flocculants [11]. The traditional multi-factor experiments that require changing one factor each time while keeping the other factors fixed is considered to be time consuming. Furthermore, the obtained results can be valid only under the fixed experimental conditions. Therefore, arriving at the same conclusion or results for another condition is uncertain. To find a solution to this problem, a design of experiment (DOE) was presented to study the effect of variables and their responses with a minimum number of experiments [12]. Response surface methodology (RSM) is the collecting of mathematical and statistical techniques that can be used for improving, developing and optimizing processes. RSM can also be used to assess relative significance of several factors, even in the case of the existence of complex interactions [13].

The aim of this study is to prepare a new hybrid inorganic-organic copolymer, indicate its characterization, and employ it as a new flocculant in wastewater treatment. The present work focuses on the use of aluminum chloride-poly(acrylamide-co-acrylic acid) hybrid copolymer, in the flocculation of wastewater by exploring the optimum conditions for the two powerful operating parameters, namely the hybrid copolymer dosage and wastewater pH.

Materials and Methods

Materials

Acrylamide (AM) was provided by AMRESCO (USA). Acrylic acid (AA) and ammonium persulfate (APS) were purchased from Shanghai Reagent Corp (China). N,N'-Methylenebisacrylamide (MBA) was supplied by Sigma (USA). N,N,N',N'-tetramethylethylenediamine (TEMED) was bought from Sinopharm Chemical Reagent Co., Ltd. (China). All other chemicals were used as received. All solutions were prepared using deionized water.

Synthesis of Hybrid Copolymer

The hybrid copolymer of aluminum chloride-poly(acrylamide-co-acrylic acid) was prepared according to the following procedures: firstly, half a mole of aluminum chloride solution prepared in 100 ml of deionized water. Next, the prepared aluminum chloride solution was moved to 500 ml three-necked flask equipped with thermostatic water bath, nitrogen line, mechanical stirrer, a reflux condenser, and a rubber septum gap were set up for the polymerization process. Then 6.8 g of acrylamide (AM) and 0.315 g of acrylic acid (AA) monomers were added at ambient temperature under continuous stirring for 30 minutes with nitrogen gas purging into the solution to remove the dissolved oxygen from the system before the polymerization took place. Later, the controlled temperature of the water bath was set at 45ºC. Then, 30 mg of the crosslinker N,N'-Methylenebisacrylamide (MBA), 30 mg of the initiator ammonium persulfate (APS) and 0.2 ml of the co-initiator N,N,N',N'-tetramethylethylenediamine (TEMED) were added to the polymerization system sequentially under atmospheric nitrogen and continuing mixing for another 30 minutes. After the polymerization was finished, the resulting product was precipitated with acetone to remove the non-reacted monomers. Finally, the produced hybrid copolymer was dried and ground into powder.

Characterization of Hybrid Copolymer

The IR spectra of the hybrid copolymer was recorded using FTIR spectroscopy (Thermo Nicolet 6700, Thermo Scientific, USA) to find the functional groups in the hybrid copolymer. The surface morphology of the hybrid copolymer was investigated by using scanning electron microscopy (SEM, Quanta 200, FEI, USA). The chemical composition of the hybrid copolymer was recorded using energy-dispersive x-ray spectroscopy (EDS) by coating the sample with gold film before analysis.

Wastewater

A wastewater sample for flocculation experiments was collected from the main sewer line in the east campus at China University of Geosciences (Wuhan, China). The sample of wastewater has the following characteristics: TSS 244 mg/l, COD 381 mg/l, pH 7.4, turbidity 295 NTU.

Flocculation Experiments

Jar-test procedures were used for the purpose of studying the activity of the hybrid copolymer in wastewater flocculation by using a programmable Jar-test apparatus (TA6, Wuhan, China). The desirable pH value of the wastewater sample was adjusted by adding either 0.1 M hydrochloric acid solution or 0.1 M sodium carbonate solution. The adjusted pH of the wastewater was done before the addition of the hybrid copolymer to the beakers of 1L. A wastewater sample was added to each jar. Subsequently, the desirable dosage of the hybrid copolymer was added to the jars with rapidly stirring 120 RPM for 60 seconds. Afterward, the stirring speed was reduced to 40 RPM and continued for 20 minutes. Thereafter, the Jar-test apparatus was powered off and the flocs in jars was allowed to settle for 30 minutes, then the samples of the supernatant were collected at the same depth for all jars (2 inches below the surface of the liquid).

The removal of the pollutants in Jar-test experiments was calculated according to the following formula:

$$Removal\ Efficiency = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \quad (1)$$

...where, C_i and C_f are the initial and final concentrations of the pollutants (TSS, COD, and turbidity).

Response Surface Methodology

Response surface methodology (RSM) was used to study the effects of pH and dosage in the flocculation process on COD, TSS, and turbidity removal from wastewater. The common type of RSM that was used was the center composite design (CCD), which is a statistical method and technique that can be used in experimental design to explore the relationship between factors and response.

The CCD used in this study was a central composite face design (CCFD) involving two different parameters: hybrid copolymer dosage and wastewater pH. A total of 13 experiments according to the three levels of factorial design were employed in the flocculation process. The design approach contained four factorial points, four axial points, one center point, and four replicated at the center point. The first factor in this study was a hybrid copolymer dosage (denoted by X_1), whereas the other factor was the wastewater pH (denoted by X_2) as shown in Table 1.

Each factor in Table 1, has three levels as codes, which are mean low level (-1), mean center level (0), and mean high level (+1). The second order polynomial equation, which represents the response surface model, is shown as follows:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \quad (2)$$

...where Y is the predicted response (COD, TSS, and turbidity removals), β_0 is constant coefficient, β_i is the coefficient of the linear term, β_{ii} is the coefficient of the square term, β_{ij} is the coefficient of the quadratic term, k is the number of factors, and X_i and X_j are the coded values of the factors.

Table 1. Design variables in the response surface methodology (RSM) of wastewater flocculation.

Variable	Factor	Unit	Real values of code level		
			-1	0	1
Dose	X_1	mg/l	80	130	180
pH	X_2	-	5	7	9

Design Expert Software was used for analyzing the experimental data by regression analysis to fit the equations developed and used for the evaluation of the significance of the statistical equations.

Results and Discussion

Characteristics of Hybrid Copolymer

The IR spectra of the hybrid copolymer were shown in Fig. 1. The peaks showed the correspondence to the functional groups in the synthesis hybrid copolymer. As shown in the figure, the peak at 2,949.80 was attributed to the O-H group whereas the peak at 1,650.24 was attributed to the C=O group. At the same time, the peak at 1,584.34 was attributed to primary amides. The peaks at 1,452.13 and 1,354.02 were attributed to C=C and C-N groups, respectively. The peak at 1,121.62 was attributed to the C-N group. Hence, results of FT-IR spectra accommodate that the hybrid copolymer of aluminum chloride-poly(acrylamide-co-acrylic acid) accomplishes synthesis and indicates the formation of the inorganic and organic compounds.

The scanning electron micrograph (SEM) image is shown in Fig. 2. It is noticed that the surface morphology of the hybrid copolymer indicated that the inorganic and organic components were homogeneously mixed in the hybrid copolymer matrix.

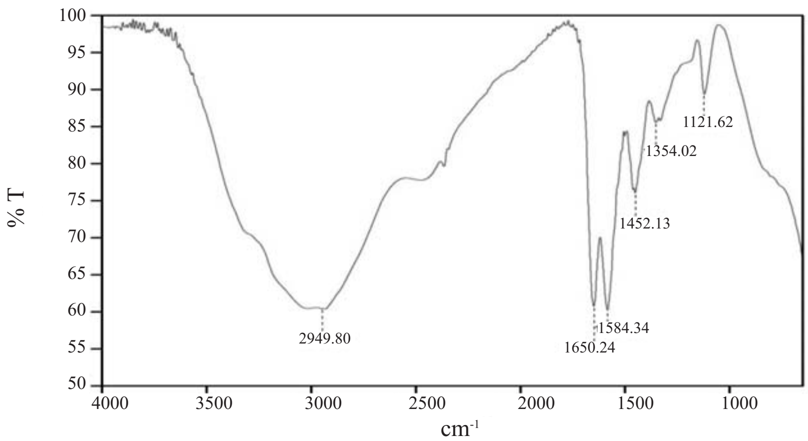


Fig. 1. FTIR spectra of the hybrid copolymer.

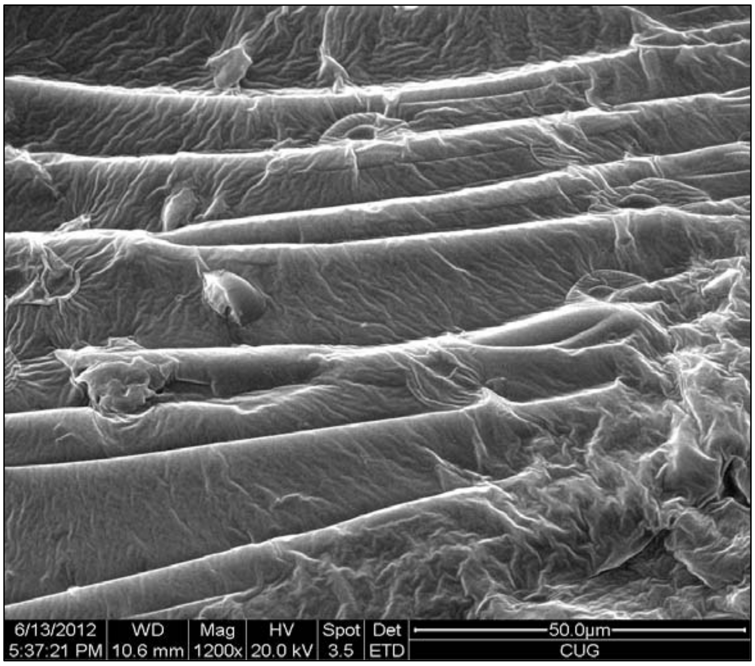
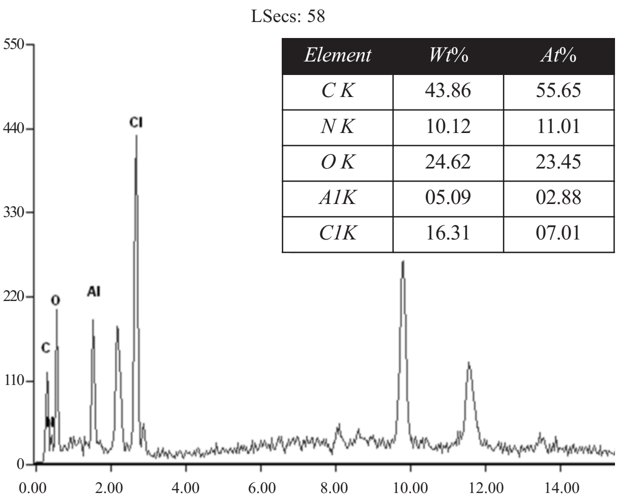


Fig. 2. Scanning electron microscopy (SEM) image of the hybrid copolymer.

The chemical composition of the hybrid copolymer was investigated by using energy-dispersive x-ray spectroscopy (EDS). Fig. 3 presents the chemical composition of the aluminum chloride-poly(acrylamide-co-acrylic acid) hybrid copolymer. It is shown that the hybrid copolymer contains 43.86% of carbon, 10.12% of nitrogen, 24.62% of oxygen, 5.09% of aluminum, and 16.31% of chloride. Thus, the distribution shows that the aluminium chloride is dispersed in the matrix of the acrylamide-acrylic acid copolymer.

Statistical Analysis

Response surface methodology was employed to find the relationship between the flocculation process responses and the two important variables as shown in Table 2.



Element	*Wt%*	*At%*
C K	43.86	55.65
N K	10.12	11.01
O K	24.62	23.45
AlK	05.09	02.88
ClK	16.31	07.01

Fig. 3. Energy-dispersive x-ray spectroscopy (EDS) for the hybrid copolymer.

According to the experimental data, the quadratic model was suggested to represent the correlation between the experimental data and all the responses because of its lowest standard deviation and p value, and its highest correlation coefficient (R^2), adjusted R^2, and predicted R^2 values. Based on the experimental data, independent variable coefficients can be calculated. These independent variable coefficients that are shown for each response (*Y*) which represent the process removal and can be obtained and given as:

$$Y_{TSS} = 98.72 + 3.93Dose + 2.73pH - 0.10Dose \times \times pH - 5.23Dose^2 - 5.23pH^2 \quad (3)$$

$$Y_{Turbidity} = 96.90 + 3.83Dose + 2.20pH - 0.33Dose \times \times pH - 5.94Dose^2 - 4.94pH^2 \quad (4)$$

$$Y_{COD} = 88.72 + 6.16Dose + 3.58pH - 0.77Dose \times \times pH - 8.16Dose^2 - 5.06pH^2 \quad (5)$$

...where *Dose* and *pH* are the quadratic model terms in coded values. The positive sign in front of the terms indicates a synergistic effect, while the negative sign indicates an antagonistic effect. The experimental data for each response were statistically analyzed by employing analysis of variance (ANOVA). The results of the ANOVA for all quadratic models were shown in Table 3. Statistically, when the p value is very low (<0.0001), it means the model is highly significant, but a p value more than 0.05 indicates that the model is usually considered as insignificant. Accordingly, the statistical data of the quadratic models in this study showed all models were significant at the 5% confidence level. Based on ANOVA results for the selected quadratic models, the terms of *Dose*, *pH*, $Dose^2$, and pH^2 were found to be highly significant ones. Whereas the term

Table 2. The central composite design (CCD) coded values of two independent variables and experimental results.

Run No.	Experimental design in Coded values		Results (removal (%))		
	X_1	X_2	TSS	Turbidity	COD
1	-1	-1	81.7	79.2	65.4
2	-1	0	89.5	87.1	75.4
3	-1	1	87.0	85.2	72.3
4	0	-1	90.0	90.6	78.2
5	0	0	99.1	97.0	89.1
6	0	0	98.9	97.1	87.8
7	0	0	98.7	97.0	89.1
8	0	0	98.7	96.9	88.9
9	0	0	99.0	96.7	88.8
10	0	+1	96.2	93.1	89.0
11	+1	-1	90.1	87.6	80.3
12	+1	0	96.7	94.6	85.6
13	+1	+1	95.0	92.3	84.1

of *Dose×pH* was not significant in all of the models under discussion.

The significant terms in the quadratic models (*Dose*, *pH*, *Dose*^{2}, and *pH*^{2}) suggest that the hybrid copolymer dosage and wastewater pH have a direct relationship with pollutant removal efficiencies. It is also noted that the interaction effect of the hybrid copolymer dosage and wastewater pH (term of *Dose×pH*) demonstrated the lowest effect on pollutant removal efficiencies. Based on the sum of squares for each individual model component, the percentages of contribution for each individual term in each model were calculated and presented (Table 4).

As shown in Table 4, the quadratic terms (*Dose*^{2} and *pH*^{2}) in the turbidity removal model demonstrated the highest level of significance with a total contribution of 58.34% as compared to the other component's effect of the first-order terms (*Dose* and *pH*) that contributed to 41.51% of the total percentage. While in the TSS removal model, the highest level of significance was noticed in the quadratic terms (*Dose*^{2} and *pH*^{2}) with a total contribution of 52.36% followed by the contribution of the first-order terms that contributed as much as 47.62%. In the COD removal model, the highest level of significance with a total contribution of 54.18% was shown in the first-order terms as compared to the other component's effect of quadratic terms with a total contribution of 45.39% of the total percentage of contribution. The lowest component contribution was noticeable in the interaction term effects, which were 0.42%, 0.01%, and 0.43% in the turbidity, TSS, and COD removal models, respectively.

The corrrelation coefficient (R^2) is used to measure the degree of fit for the model. The desirable value of R^2 is close to 1, which means better correlation between the experimental and predicted values [14]. The adjusted coefficient of determination (*adj.* R^2) is used to compare the models with different numbers of independent variables [15]. The adjusted R^2 value of (0.9922) in the ANOVA table result for TSS removal suggests that the total variation of

Table 3. Analysis of variance (ANOVA) results for response surface quadratic models.

Sources	Turbidity removal			TSS removal			COD removal		
	F-value	p-value	Rermark	F-value	p-value	Rermark	F-value	p-value	Rermark
Model	185.37	<0.0001	a	306.57	<0.0001	a	68.63	<0.0001	a
Dose	213.64	<0.0001	a	372.31	<0.0001	a	110.32	<0.0001	a
pH	70.37	<0.0001	a	179.79	<0.0001	a	37.45	0.0005	b
Dose × pH	1.02	0.3453	c	0.16	0.7007	c	1.17	0.7007	c
Dose^2	235.97	<0.0001	a	303.52	<0.0001	a	89.41	<0.0001	a
pH^2	163.19	<0.0001	a	303.52	<0.0001	a	34.38	<0.0001	a
Lack of fit	40.53	0.0019	b	16.85	0.098	b	15.05	0.0121	b
Model statistics									
R^2	0.9925			0.9955			0.9800		
Adj. R^2	0.9872			0.9922			0.9657		
Pred. R^2	0.9264			0.9643			0.8107		
Adeq P.	39.489			50.809			24.353		

R^2– correlation coefficient; Adj. R^2– adjusted R^2; Pred. R^2– predicted R^2; Adeq.P – Adequate precision; a – high significant; b – significant, and c – not significant

Table 4. Percentage of contributions (PC) for each individual term in response quadratic models.

Sources	Turbidity removal		TSS removal		COD removal	
	SS	PC%	SS	PC%	SS	PC%
Dose	88.17	31.23	92.83	32.11	226.94	40.45
pH	29.04	10.28	44.83	15.51	77.04	13.73
Dose×pH	0.42	0.15	0.04	0.01	2.40	0.43
Dose^2	97.38	34.49	75.68	26.18	183.92	32.78
pH^2	67.34	23.85	75.68	26.18	70.72	12.61
Total	282.36	100	289.04	100	561.02	100

99% for TSS removal was assigned to the independent variables and only about 1% of the total variation cannot be explained by the model. However, in terms of turbidity and COD removal the total variations that cannot be explained by their model are only about 2% and 4%, respectively. Adequate precision is used for comparing the range of the predicted values at the design points to the mean prediction error [16]. Adequate precision greater than 4 indicated adequate model favoritism. Since all adequate precision values are more than 4, this indicates an adequate signal for all removal models.

Flocculation Process Analysis

The surface plot (Fig. 4a) represented the maximum removal of turbidity in the quadratic model that showed more than 95% of turbidity removed with the hybrid copolymer dosage range from (140-160 mg/l) and wastewater pH range from 7.2 to 8.3. This phenomenon can be explained as follows: within optimum pH, the hybrid copolymer can easily neutralize the residual charge on the particles and in that range, the hybrid copolymer expands the chain of bridging. Fig. 4b represents the surface plot for TSS removal with a maximum removal of more than 98% with a hybrid copolymer dosage range from 120 mg/l to 175 mg/l and wastewater pH range from 6.4 to 8.7. This maximum removal efficiency can be explained by the fact that the aluminum chloride in the hybrid copolymer has limited solubility as a result of the precipitation of an amorphous hydroxide, which may play a significant role in determining the efficiency of the flocculation process.

It is noticeable that the removal efficiency trend for both TSS and turbidity are likewise, because the turbidity removal in wastewater fluctuated consequently to the TSS removal [17]. It was noticed that removal efficiency decreases when moving away from these pH ranges, meaning decreasing of the response. The removal reduction was found in the alkaline region, especially when the pH is more than the optimum value, and the removal of both TSS and turbidity will decrease due to the adsorption of aluminum hydroxide onto wastewater particles.

The COD surface plot (Fig. 4c) indicates that the maximum removal efficiency is more than 88% when the hybrid copolymer dosage range 120 mg/l to 175 mg/l and wastewater pH range from 6.4 to 9.0. It is noticed that COD removal efficiency will decrease when pH increases beyond the optimum pH range. This reduction in COD removal is due to the fact that in an alkalinity region, the aluminum hydroxide complexes in the hybrid copolymer will start to form and then lead to an increase in Al^{3+} ion or OH^- ion that leads to an increase in the solubility constant of aluminum hydroxide.

Hence, any increase in the hybrid copolymer dosage after the optimum pH range will not notice any further COD reduction. This is because almost all CODs were removed at that stage. This phenomenon will aid in turbidity and TSS removal efficiences by increasing the flocs size and quantity and then increasing the TSS and turbidity removal processes.

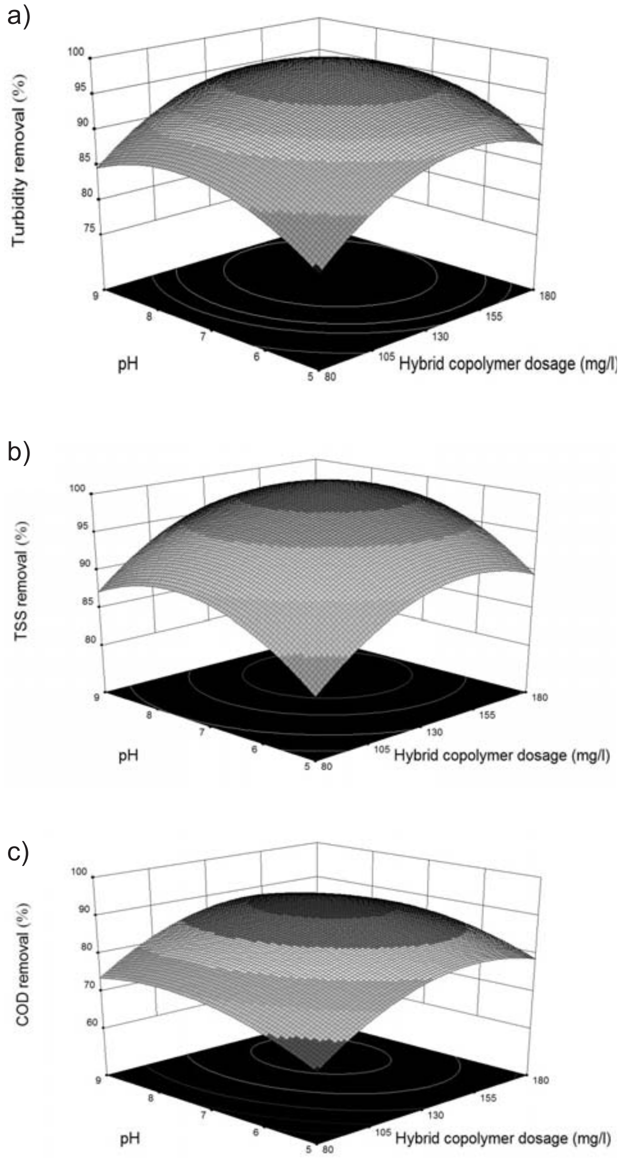


Fig. 4. 3D surface plot for (a) turbidity removal, (b) TSS removal, and (c) COD removal.

Optimization Condition and Verification

A desirable function was used to explore the optimum condition of the two variables, which are hybrid copolymer dosage and wastewater pH in this study. The desirability function is commonly used in RSM to find a combination of variables and to optimize the multiple response [18]. Desirability function was set as follows: maximum process removal with a minimum range of hybrid copolymer dosage and within the pH ranged from 5 to 9. The search in the attempt of 39 starting points results from the optimization of RSM, showing the best maximum removal efficiencies for COD, TSS, and turbidity removals, which were 88.6%, 98.6%, and 97%, respectively. These optimum removals were acquired as a desirability function of 0.846 with the hybrid copolymer dosage of 125 mg/l and with a wastewater pH of 7.55.

Finally, under optimum conditions, two additional experiments were conducted to verify the validity of the statistical experimental strategies. The obtained removal results of these two experiments were close to those estimated by using the response surface methodology model. This proved that the model developed was considered to be accurate and reliable.

Conclusions

In this research, a novel hybrid copolymer of aluminum chloride-poly(acrylamide-co-acrylic acid) was successfully synthesized using the free radical polymerization method. The novel hybrid copolymer was characterized by FTIR, EDS, and SEM. The characterization results have shown the functional groups, morphology, and the chemical composition of the novel hybrid copolymer.

Flocculation process was applied to investigate the effect of hybrid copolymer dosage and wastewater pH on the removal of COD, TSS, and turbidity from wastewater. The RSM approach, which uses CCD, was employed to formulate a mathematical model and optimize the flocculation process parameters for COD, TSS, and turbidity removals. The results of the formulated models show clearly that the COD, TSS, and turbidity removal efficiencies using hybrid copolymer was severely influenced by initial wastewater pH and hybrid copolymer dosing.

On the other hand, the mathematical models were analyzed using ANOVA. The results of ANOVA show that the models were satisfactorily adjusted to the experimental data. The optimization showed that the maximum COD, TSS, and turbidity removal efficiencies were obtained at initial wastewater pH and hybrid copolymer dosage of 7.55 and 125 mg/l respectively. RSM proved to be a powerful tool in the optimization of the flocculation process for COD, TSS, and turbidity removals from wastewater, and the synthesis hybrid copolymer can be used as an alternative solution for conventional coagulants/flocculants that are used in wastewater treatment.

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