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Response surface methodology (RSM) for wastewater flocculation by a novel ($AlCl_3$-PAM) hybrid polymer

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Abstract. In this study, a novel aluminum chloride-ploy(acrylamide) hybrid polymer has been synthesized by free radical solution polymerization of acrylamide (AM) onto aluminum chloride ($AlCl_3$) in the presence of ammonium persulphate and sodium hydrogen sulphite as polymerization's initiators. On the other hand, the structure of hybrid polymer ($AlCl_3$-PAM) has been characterized by Fourier transform infrared spectroscopy (FTIR). The central composite design (CCD) and response surface methodology (RSM) have been applied in the flocculation process of wastewater treatment to achieve maximum removal efficiencies of total suspended solids (TSS), turbidity , and chemical oxygen demined (COD), as the other objectives of this study. The operating variables in this experiment were new hybrid polymer dose and wastewater pH. The maximum conditions have been found to be wastewater pH 7, and hybrid polymer dose 100 mg/l. Under these optimal conditions, the removal of turbidity, TSS, and COD in the effluent have been reached to 98.2%, 99.1%, and 90.6% respectively. According to these results, domestic wastewater treatment using ($AlCl_3$-PAM) has proved to be an effective alternative in the administration of COD, TSS, and turbidity problems of municipality wastewater.

Introduction

Science is continually progressing, so one should expect improvement of scientific processes of the coagulation-flocculation treatment processes and develop new coagulants/flocculants. Coagulation-flocculation process has a wide range of applications in water and wastewater treatment units because it is efficient and simple to operate [1,2]. It is used for removing turbidity, organic matters, colors and microorganisms. Coagulation-flocculation is a proven technique for the treatment of high suspended solids wastewater [3].

The coagulants widely used in wastewater treatment facilities are aluminum and iron salts because of their broad range of contaminations' removal efficiency on destabilizing dissolved and colloid contaminations and production of large floc aggregates. Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate called "sweep flocculation"[4]. The relative importance of these mechanisms and the effectiveness of the coagulation-flocculation process and its operation costs depend on the type of coagulant used, its concentration, and the pH of the water. In most cases, it is necessary to determine them empirically [5].

The enhancement formation of large aggregates (flocs) in the removal of wastewater pollutants by flocculation can be occurring by two general mechanisms [6], which are charge patching and bridging.

The new research is concerned with the development and synthesis of novel composite or hybrid coagulant/flocculent, which is a mixture of both inorganic and organic materials. Inorganic Polymeric Coagulants or Flocculants (IPFs) refer to the widely used regents in water and wastewater [7].

The addition of inorganic salts to the organic flocculants was suggested as the main method for preparing hybrid-flocculating polymers [8, 9]. The goal of the method of preparing hybrid polymer is to enhance the aggregating power of flocculants by increasing the ratio of effective component and positive charge of flocculants [9, 10].

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that is useful for improving, developing and optimizing processes , and it can be used to evaluate relative significance of several affecting factors even in the presence of complex interactions[11,12]. RSM is used for designing experiments, building models, evaluating the effects of various factors and searching optimum conditions for desirable responses and reducing number of experiments [13].

The objective of this study is to synthesize a novel hybrid polymer and show its chemical structure through using FTIR test. This research aims at using this polymer in wastewater treatment application and analyzing the effects of the experiment factors, including hybrid polymer dose, and initial pH on the flocculation process which was optimized by RSM.

Experimental

Materials. Acrylamide (AM) were purchased from Amresco. Ammonium persulphate (AMP) was bought from Xi'an Reagent Factory. Sodium bisulfite supplied by Shanghai Chemicals Reagent Corp. Acetone used was of analytical regent grade.

Preparing of hybrid polymer. First, Acrylamide (AM) monomer (7.108 g in 100 ml of deionized water) was prepared in a 500 ml three-necked flask equipped with thermostatic stirring water bath, nitrogen line, mechanical stirrer, a reflux condenser, and a rubber septum gap was set up for the polymerization. The controlled temperature of the water bath was set up at 50° C. along the polymerization process. The acrylamide monomer solution was purged with nitrogen for 30 minutes to remove the oxygen dissolved from the system before the polymerization took place. To initiate the polymerization process, a redox initiator , 4.6 mg of ammonium persulphate (APS) and 0.52 mg of sodium hydrogen sulphite were added [9,11]. The polymerization reaction was set at 50° C for 2 h. , then one and a half equivalent mole of aluminum chloride was added to the polymerization flask under mechanical stirrer for 4.5 h under atmospheric nitrogen. The resulting gel product was precipitated with acetone to remove the non-reacted acrylamide. The final hybrid polymer was then vacuum dried and grounded into powder.

Characterization of hybrid polymer. To investigate the characterization of the hybrid polymer, FTIR test was done. The spectroscopic analysis of the hybrid polymer was recorded on a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, USA) by using KBr pellets. The spectra were accumulation of 36 scan with a resolution of 2 cm^{-1} and a spectral range of 4000-400 cm^{-1}.

Wastewater samples. The wastewater samples for these experiments were collected from the sewer system network in the China University of Geosciences (CUG). The wastewater samples were transported to the lab within 20 minutes and then characterized there for COD, Turbidity, pH, and total suspended solids. The initials wastewater values for COD, turbidity, pH, and total suspended solids were 330 mg/l, 249 NTU, 7.6, and 197 mg/l respectively.

Jar Test. Flocculation experiments were carried out in the programmed jar test apparatus (TA6 , Wuhan , China) at the room temperature. The initial wastewater pH was adjusted by using 0.5M HCL and 0.5M NaOH. When the wastewater samples of 500 ml transferred to the beakers, $AlCl_3$-PAM hybrid polymer was added to each beaker. The aqueous solution was then stirred rapidly and mixed at a paddle speed of 120 rpm for 1 minute followed by slow mixing at 30 rpm for 20 minutes. Finally, the treated samples were allowed to settle for 30 minutes.

The removal of the studied parameters in these experiments was calculated by applying the following formula (Eq. 1):

$$\text{Removal Efficiency} = \left[\frac{C_0 - C_i}{C_0}\right] \times 100 \quad (1)$$

Where, C_0 and C_i are the initial and final concentrations of the studied parameters.

Experimental design and analysis

Response surface methodology (RSM) is a statistical method which is frequently used in the experiment designs because it can be used in optimization processes. The version of the design-expert software (version 8.0.0.5, State-Ease, Inc., USA) was used to optimize the major operating factors ($AlCl_3$-PAM hybrid polymer dose and wastewater pH). In this study, the Center Composite Design (CCD) and RSM were applied to find out the effective variables functioning on the flocculation efficiency for chemical oxygen demand (COD) , total suspended solids (TSS) , and turbidity removal as response (depended variables).

In this study, RSM used the common form of CCD, which is Center Composite Face Design (CCFD) that consists of 2^k factorial points (k means factors=2) , 2k axial points and five replicated at center point provide estimation of experimental error variance.

The independent variables (factors) were hybrid polymer dose (X1) and wastewater pH (X2). These factors have three levels as follows: -1 (low), 0 (center), and +1 (high) as shown in table (Table 1). The actual values of coded levels of factors were obtained according to preliminary experiments and these codes are included in table (Table 1).

Table 1. The three levels of the Experimental factors

Design variable (Factor)	Symbol	Real values of coded levels		
		-1	**0**	**+1**
Hybrid polymer dose (mg/l)	X1	40	70	100
Wastewater pH	X2	5.5	7	8.5

The empirical second order polynomial equation (Eq. 2) is used to prove the relationship between the factors (X1 and X2) and the investigated responses (Y1, Y2, and Y3).

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

Where Y is the response equation (COD removal, TSS removal, and turbidity removal); β_0 constant coefficient; β_i is coefficient of linear term; β_{ii} is coefficient of square term; β_{ij} is coefficient of quadratic term. k is the number of independent variables. X_i and X_j are the coded values of independent variables.

Results and Discussion

FTIR Spectra. The infrared spectrum of the hybrid polymer ($AlCl_3$-PAM) is shown in figure (Fig. 1). According to the IR spectra of $AlCl_3$-PAM hybrid polymer, the high peak was at 3381 cm^{-1}, that is corresponding to primary amine $–NH_2$, primary amides, and aromatic amine, whereas the low peak of 2360 cm^{-1} is corresponding to the amine. The sharp peak at 1631 cm^{-1} is representing the primary amides. The low peak at 1451 cm^{-1} is corresponding to $–CH_2$ and $–CH_3$. The low peak at 1329 cm^{-1} is attributed to the $–CH_3$, whereas the low peak at 1115 cm^{-1} is contributed to the $–C–NH_2$. In addition, the broad and low peaks are at 629 cm^{-1} ,which is attributed to the axial pond of C–Cl. The IR analysis results indicated the occurrence of polymerization for acrylamide monomer on $AlCl_3$ and the resulting product was a hybrid polymer of $AlCl_3$-PAM and it is an inorganic-organic complex.

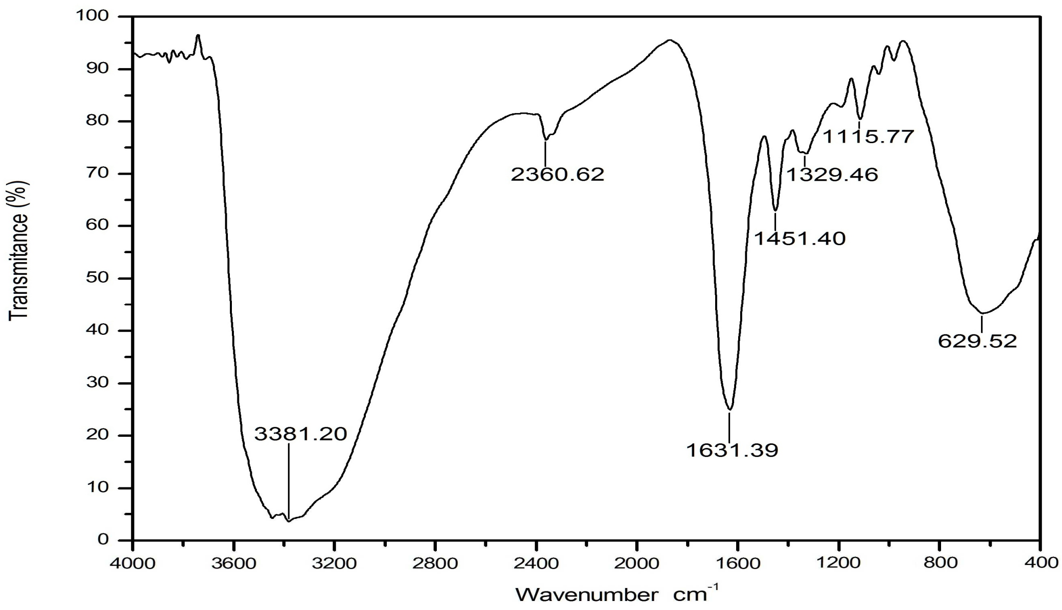


Fig. 1 FTIR spectra of ($AlCl_3$-PAM) hybrid polymer.

Statistical analysis. A total of 13 experiments were done to determine each response coefficients for independent variables as shown in table (Table 2). Several models were used to obtain the regression equation for each response and it was also used to find out the correlation of the experimental data. According to the sequential model sum of square, lack of fit tests, and model summary statistics, it was found out that the quadratic model was the best. Hence, it was suggested as a model for all responses because it has been proved that it is what fits most to experimental data with the lowest standard deviation and P value, highest correlation coefficient, adjusted R^2, predicted R^2 values. As a result, this model was adopted. The cubic model was aliased because there were insufficient points to estimate the model coefficients. The final quadratic model for each response (Y1, Y2, and Y3) in term of coded factors is shown in equations (Eq. 3, Eq. 4, and Eq. 5) :

$$Y1 = 98.04+8.57A+4.48B-0.3AB-6.78A^2-6.13B^2 \tag{3}$$

$$Y2 = 96.09+10.10A+3.2B-0.45AB-7.08A^2-8.08B^2 \tag{4}$$

$$Y3 = 86.68+8.93A+2.22B+1.28AB-3.77A^2-7.52B^2 \tag{5}$$

Where Y1, Y2, and Y3 are the response (dependent variables) of TSS, turbidity, and COD removal efficiency respectively. Whereas A and B are the coded factors (independent variables) of hybrid polymer dose and wastewater pH respectively.

Table 2. Experimental design and responses

Run no.	Experimental design		Response (results)		
	X1: Polymer dose (mg/l), (code)	X2: pH value , (code)	TSS Removal (%)	Turbidity Removal (%)	COD Removal (%)
1	70 (0)	5.5 (-1)	86.2	83.2	75.8
2	70 (0)	7 (0)	98.0	96.7	87.4
3	70 (0)	8.5 (+1)	96.5	90.2	79.6
4	40 (-1)	5.5 (-1)	72.3	68.2	66.2
5	70 (0)	7 (0)	98.4	96.7	87.5
6	100 (+1)	7 (0)	99.1	98.2	90.6
7	100 (+1)	8.5 (+1)	97.9	94.1	88.6
8	70 (0)	7 (0)	98.1	96.5	87.2
9	70 (0)	7 (0)	98.2	97.4	86.8
10	70 (0)	7 (0)	98.6	95.8	87.4
11	40 (-1)	8.5 (+1)	81.2	75.2	68.4
12	40 (-1)	7 (0)	82.3	77.2	72.3
13	100 (+1)	5.5 (-1)	90.2	88.9	81.3

Analysis of variance (ANOVA). The final results of the quadratic model for each response were analyzed by ANOVA to assess the "goodness of fit". The empirical equations (Eq. 3, Eq. 4, and Eq. 5) have some statistically non-significant values that have lowest F value; therefore, there is need to eliminate these terms from the response equations. The P value (P>Prob) in the terms of each response equation for (TSS, turbidly, and COD removals) models are more significant and have the probability (p-value) of 95% confidence level except in the interaction terms in each TSS and turbidity are not significant because it is more than 0.1.

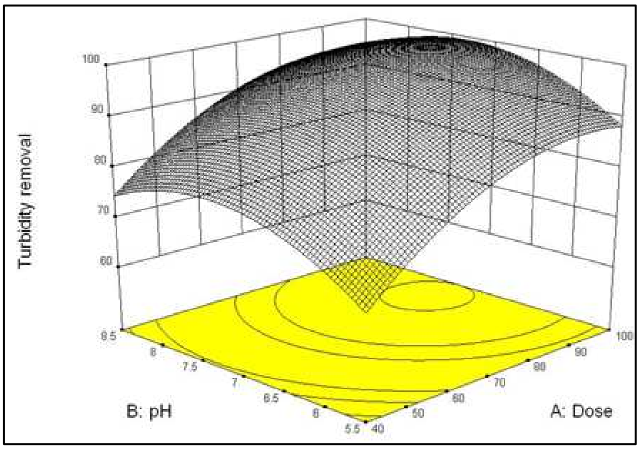
The measure of how much variability in observed response value can be explained by experimental variable and their interaction is called R^2. The closer R^2 to 1, the better the model predicts the response [14]. The value of R^2 for (TSS, turbidity, and COD removals) have been 0.996, 0.989, and 0.984 respectively. Of course this indicates that there are high dependence and correlation between the observed and predicted values of the response. The adj. R^2 of (TSS, turbidity, and COD removals) have been 0.994,0.983, and 0.973 respectively, so it is very close to R^2 for each response equation then the predication of experimental data is considered to be satisfactory.

The values of adj. R^2 for TSS, turbidity, and COD removals models, suggested that the total variation be of about (99%,98%, and 97%) for TSS , turbidity, and COD removals respectively. This can be attributed to the independent variables and there is only about (1% ,2%, and 3%)of the total variation that cannot be explained by the (TSS, turbidity, and COD Removals) models.
The measures of the adequate precision for the response models are (58.92, 35.71 , and 28.29). These are the measures of the signal to noise ratio, when this ratio greater than 4, is generally desirable [15]. The coefficient of variance (CV) , is the ratio of the standard error of estimate to the mean value of observed model (represented as %), when CV value is less than 10% , the model can be normally considered reproducible[16]. The low CV values of the models (0.76, 1.47, and 1.68) indicate that the precision and reliability of experiments are good.

Flocculation process analysis. The effects of experimental factors on the response were examined by the design-expert software as 3D surface and contours plots for the model (Eq. 3, Eq. 4, and Eq. 5) and the graphs displayed in figures (Fig. 2, Fig. 3, and Fig. 4) that show the responses of experimental variables, and these graphs can be used to identify the major interaction between the variables.

The 3D surface plot (Fig. 2.a) and contour plot (Fig. 2.b) for turbidity removal show the optimum range for pH (6.5-8) and hybrid polymer dose range of (70-100 mg/l). The maximum removal of turbidity are found to be with that optimum pH region, because in that pH, the hybrid polymer $AlCl_3$-PAM becomes an ionized state, and the ionized Al^{3+} can easily neutralize charge residual on particles and expend the chain on the bridge.

One can also notice that the increase in pH is accompanied by flocculation decrease. This is due to the start of $Al(OH)_3$-PAM complexes in the alkaline region that lead to the adsorption of $Al(OH)_3$-PAM onto wastewater particles.



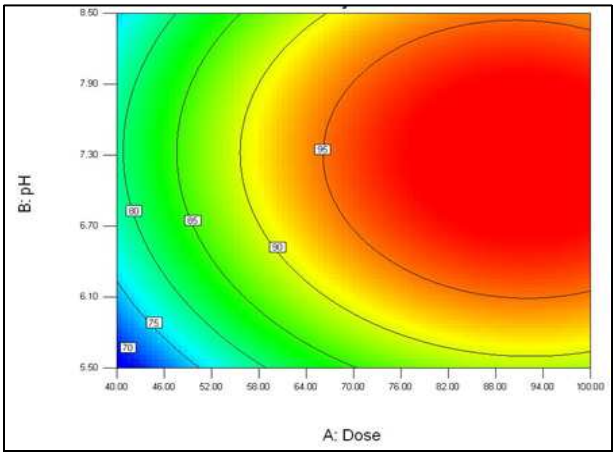


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Fig. 2 3D surface plot (a) and contour plot (b) for Turbidity removal.

The 3D surface plot (Fig. 3.a) and contour plot (Fig. 3.b) for COD removal show that the optimum COD removal was in the pH range of (6.5-7.5) and hybrid polymer dose range (70-100 mg/l). The COD reduction in alkalinity (pH more than the optimum value) because there is increase of $Al(OH)_3$-PAM complexes that start to form because the formation of aluminum hydroxide precipitates at alkalinity and any increase in Al^{3+} ion or OH^- ion makes the solubility constant of the aluminum hydroxide increase too. The maximum removal of COD is in pH value that almost all

aluminum ions are converted into perceptible hydroxide [17]. Beyond that optimum pH value, the COD removal decreases probably due to the increase in solubility of the aluminum precipitate.
The increasing of $AlCl_3$-PAM hybrid polymer dose after optimum pH range is accompanied by no further COD removal because almost all the COD is removed at this stage. The presence of excessive $AlCl_3$-PAM dose forms too much flocs and increases the turbidity and total suspended solid removal.

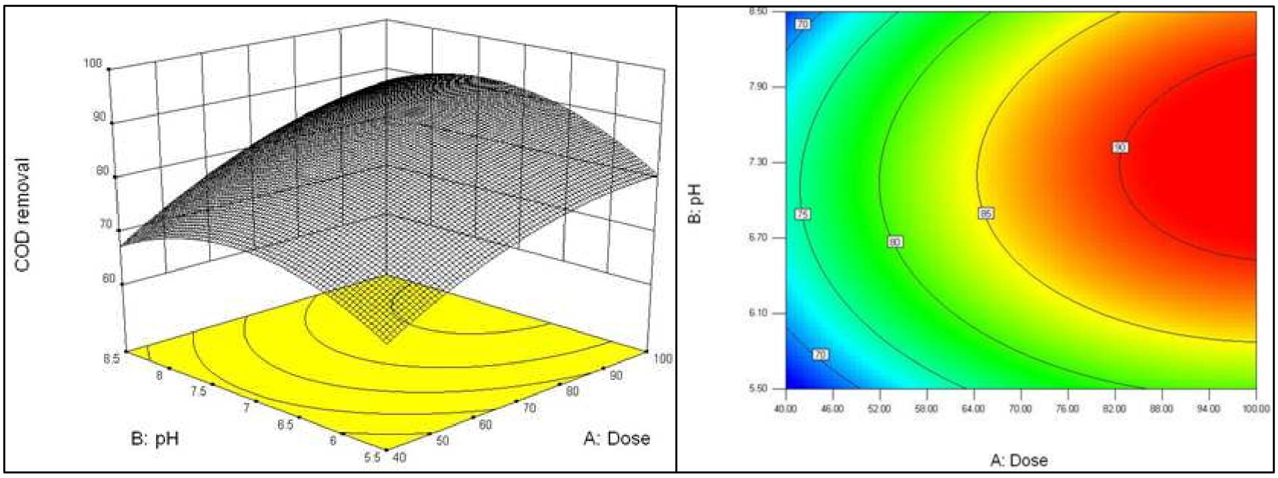

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Fig. 3 3D surface plot (a) and contour plot (b) for COD removal.

The 3D surface plot (Fig. 4.a) and contour plot (Fig. 4.b) show the optimum TSS removal lay in the pH range of (6.5-8) and dose of (70-100 mg/l) . The increase in the hybrid polymer dose will increase the TSS removal because it is associated with "bridging" flocculation mechanism. It is supposed that in this case particles absorb on the solid surface and form "loops" and "tails" which are of substantial dimension that can form "bride" between different particles [18]. The removal trends of TSS are similar to those of turbidity removal trends because the turbidity removal of wastewater fluctuates according to TSS removal [19].

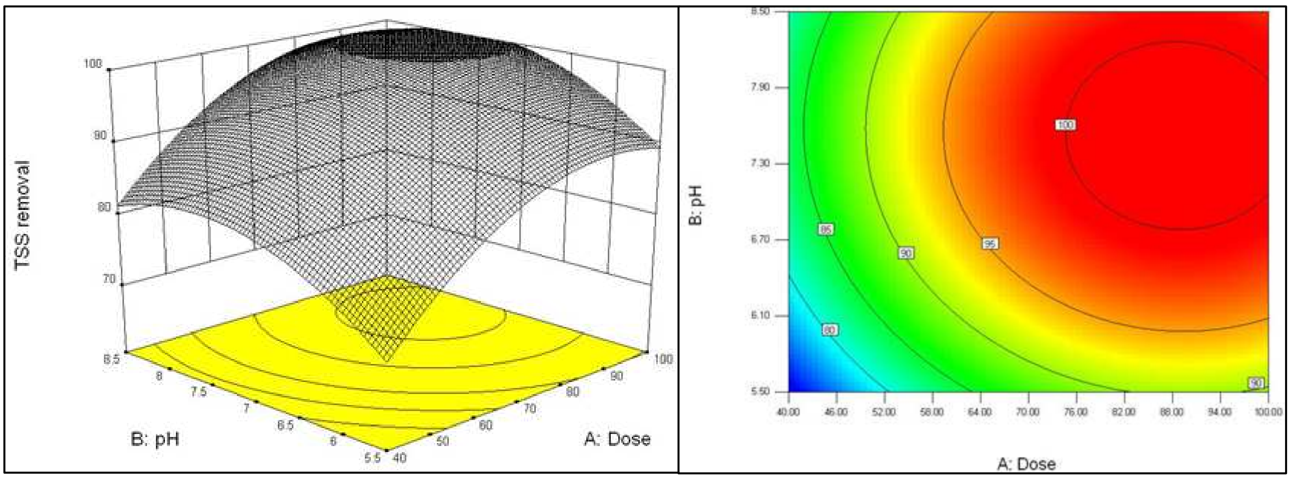

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Fig. 4 3D surface plot (a) and contour plot (b) for TSS removal.

Optimization of the flocculation process. The determination of optimum values of the variables in the flocculation process is the main objective of the optimization method. Maximum removal efficiencies for TSS, turbidity, and COD were graphically optimized by using the design-expert software. The desired goal in optimization of our flocculation experiments is to maximize the TSS, turbidity, and COD removal, and to keep the operation variables (hybrid polymer dose and pH) within its range. As far as the optimization condition and the maximum response of (TSS, turbidity, and COD) are concerned , it was found that the value of desirability function was 0.901. From that high desirable function, the optimum of the working condition and respective removal efficiency is (hybrid polymer dose =100 mg/l, pH=7.31, TSS removal efficiency= 100%, Turbidity removal efficiency= 99.34%, and COD removal efficiency = 92.24%).

After that, an additional experiment was done according to the optimum variables to check the verifying of flocculation efficiency for TSS, turbidity, and COD removal. From that additional experiment, the TSS removal efficiency was 99.5% and turbidity removal efficiency was 99.2% , and the COD removal efficiency was 90.9%. These results were found to agree with what was predicted by the model, and RSM is proved to be a powerful tool for the optimization of operational condition in the flocculation efficiency.

Conclusion

The fast process of wastewater treatment is physical-chemical methods; one of these methods is the coagulation flocculation in which many types of commercial and conventional coagulants can be used. In this study, a new hybrid polymer has been synthesize and used to treat the wastewater. This novel polymer has been accomplished by focusing on the influence of operating variables: hybrid polymer dose, and wastewater pH using RSM with CCD. The results arrived at by applying this model have been verified by conducting the analysis of variance (ANOVA). Effects of both hybrid polymer dose and wastewater pH on the optimal operational conditions are : initial pH value of 7.31 and the hybrid polymer dose of 100 mg/l and under such conditions, the removal efficiencies were 92.2 %, 100 %, and 99.34 % for COD , TSS ,and turbidity respectively. By applying these parameter values, wastewater removal has been predicted and confirmed experimentally.

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