Response surface modeling of polyacrylamide redox polymerization

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Abstract: Polyacrylamide was obtained through redox polymerization in a single batch reactor. Redox initiators, consisting of ammonium persulphate and sodium bisulfite, were applied in initiating the redox polymerization. Response surface methodology (RSM) was used to optimize the polymerization process. Four design parameters i.e. temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite were taken into account for optimization. An empirical model was constructed in terms of related significant design parameters to describe the polyacrylamide conversion (%) as the response. Based on the response surface plots and analysis of variance (ANOVA), optimum redox polymerization obtained was: 1.0335M acrylamide, 5×10^{-4} M ammonium persulphate and 1×10^{-4} M sodium bisulfite under 65°C, producing 96.89% of polyacrylamide in 10 minutes. FT-IR, GPC and TEM analysis were carried out to investigate the changes of chemical functional groups and molecular structure during the conversion of acrylamide to polyacrylamide. The weight average molecular weight of the polyacrylamide produced was 1.66×10^{6} Da. Vinyl group, which existed in acrylamide FT-IR spectra, disappeared during the conversion of acrylamide into polyacrylamide, and it was replaced by a new alkyl group. The viscosity of aqueous polyacrylamide solution increased with the concentration. Polyacrylamide was observed in linear tree-roots-like structure under TEM viewing.
Keywords: Polyacrylamide, optimization, redox polymerization, response surface methodology.

Introduction

The production of polyacrylamide has received extensive attention due to their wide applications in wastewater treatment[1,2,3,4,5,6,7,8,9]. Redox polymerization is one of the effective methods used in polymerizing acrylamide. This method requires lower activation energy compared to that of thermal polymerization. It is able to produce a high molecular weight polymer with high yield[10,11].

One problem associated with this redox polymerization technique is the determination of the optimal condition of the process which will produce the highest yield. There are many factors that have to be optimized; amongst them are concentration of monomer, concentration of the redox initiators and temperature. The conventional method of determining the best condition was by using the univariate method whereby the experiment was carried out by varying one factor while keeping all other factors fixed at a specific set of conditions[12]. However, the shortcomings of this single-dimensional analysis method were that they were laborious and, time and resource consuming; and the real optimal range may not be obtained, since the interactions between factors were not considered. In order to overcome these shortcomings, response surface

methodology (RSM) is proposed to be employed in this study. RSM is a collection of mathematical and statistical techniques that is used to investigate the effects of several design parameters at different levels as well as their interactions simultaneously[13]. RSM has been proven to be an effective technique to determine the optimal operating condition, by evaluating the effects of several design parameters and their interactions on the responses with a limited number of planned experiments[12,14]. Therefore, it is extensively used for scientific and technical application optimization in applied chemistry and physics, biochemistry and biological, chemical engineering and environmental protection[14,15,16,17].

In this research, central composite design, which is one of the standard designs in RSM, was used to determine the optimum redox polymerization condition for polyacrylamide. Four design parameters: temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite, were taken into account as the independent variables while polyacrylamide conversion (%) was the response (dependent variable). The experimental output was analyzed using Minitab 14 software. The optimal redox polymerization condition was determined at the highest percentage conversion of polyacrylamide. An empirical model was constructed based on the related significant independent terms and their interactions to describe the response surface. The fitness of the proposed model was then determined using analysis of variance (ANOVA). The constructed response surface model was used to determine the optimal condition.The optimized polyacrylamide was characterized using FT-IR, GPC and TEM to investigate the changes of chemical and molecular structure during the conversion of acrylamide to polyacrylamide. Molecular weight and solution viscosity of the optimized polyacrylamide were also studied.

Experimental

Materials

Acrylamide (AM) (>99% purity, Merck) was used without further purification. Ammonium persulphate (AR, Systerm) and sodium bisulfite (GR, Acros Organics) were used as redox initiators. Deioinized water was used throughout the experiment.

Redox polymerization

Acrylamide was polymerized using a single batch reactor consisting of a 500 mL three-necked reaction flask equipped with a reflux condenser, a thermostatic stirring water bath and an oxygen-free-nitrogen gas inlet. Acrylamide solution with concentrations of 0.64 M – 1.12 M were transferred into the reaction flask and thoroughly stirred. Oxygen-free-nitrogen gas was purged into the acrylamide solution for 10 minutes to deoxygenate the solution. The temperature of the thermostatic stirring water bath was controlled to attain equilibrium temperatures ($45^{o}C$ – $65^{o}C$) before the redox polymerization took place. To initiate the redox polymerization, certain concentrations of ammonium persulphate ($1x10^{-4}$ M – $5x10^{-4}$ M) and sodium bisulfate ($4x10^{-5}$ M – $8x10^{-5}$ M) were injected into the acrylamide solution. The redox initiation system follows the reactions[10,11]:

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- \cdot + HSO_3 \cdot \qquad (1)$$
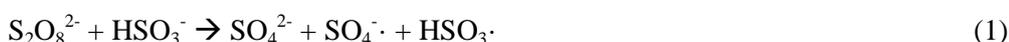
The addition of reducing agent (sodium bisulfite) in the initiation system helps in decomposing ammonium persulphate into persulphate ion. Hence, the radical formation and polymerization process can be accelerated[10]. Redox polymerization was carried out for 10 minutes after the redox initiator couple have been injected into the acrylamide solution. The polymerization process was terminated after 10 minutes of polymerization. The polymerized acrylamide solution was precipitated with cold acetone to obtain polyacrylamide. The precipitated polyacrylamide was separated by filtration and dried in an oven at $150^{o}C$ until it attained a constant weight. The conversion was determined through the following equations:

$$\text{Conversion (\%)} = \frac{\text{polyacrylamide obtained (g)}}{\text{feed acrylamide (g)}} \times 100\% \qquad (2)$$

Experimental design and analysis

Central composite design (CCD) which is one of the standard designs of RSM was employed in optimizing polyacrylamide redox polymerization[18]. The design parameters are usually described in different units and different limits of variation. The significance of the design parameters on response is then compared after they are coded. In CCD, design parameters were coded as x_i where x_1 represents concentration of

acrylamide, x_2 represents concentration of ammonium persulphate, x_3 represents concentration of sodium bisulfite and x_4 represents polymerization temperature. The real values of the design parameters, shown in Table 1, were determined through the following equation:

Table 1 Levels of variable tested in the 2^4 central composite design.

Variables	Range and levels				
	-2	**-1**	**0**	**1**	**2**
x_1: concentration of acrylamide (M)	0.64	0.76	0.88	1.00	1.12
x_2: concentration of ammonium persulphate (M)	0.0001	0.0002	0.0003	0.0004	0.0005
x_3: concentration of sodium bisulfite (M)	0.00004	0.00005	0.00006	0.00007	0.00008
x_4: polymerization temperature (°C)	45	50	55	60	65

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

where x_i is the coded value of the ith test variable; X_i is the uncoded value of the ith test variable, X_0 is the value of X_i at the center point of the investigated area and δX is the step change. The central composite design which consists of a 2^4 factorial design with 4 center points, 8 augmented axial points coded $\pm\alpha$ and 2 axial center points (all design parameters at zero level), is shown in Table 2. The value of α was calculated as follows:

Table 2 Central composite design and response for acrylamide redox polymerization.

Runs	Design parameters				Response
	AM (x_1)	$(NH_4)_2S_2O_8$ (x_2)	$NaHSO_3$ (x_3)	Temperature (x_4)	Conversion (%)
1	1	1	-1	1	60.35
2	1	-1	1	1	47.91
3	1	-1	1	-1	37.24
4	1	1	-1	-1	42.75
5	0	0	0	0	39.37
6	1	-1	-1	1	42.19
7	1	-1	-1	-1	29.38
8	-1	-1	-1	1	33.51
9	-1	-1	1	1	36.74
10	-1	-1	1	-1	26.22
11	-1	1	1	-1	36.02
12	0	0	0	0	39.74
13	1	1	1	1	68.39
14	0	0	0	0	40.04
15	1	1	1	-1	50.10
16	-1	1	-1	1	47.64
17	-1	1	-1	-1	32.34
18	0	0	0	0	38.54
19	-1	1	1	1	52.21
20	-1	-1	-1	-1	23.25
21	-2	0	0	0	28.41
22	2	0	0	0	52.71
23	0	-2	0	0	24.70
24	0	2	0	0	52.56
25	0	0	-2	0	35.39
26	0	0	2	0	46.91
27	0	0	0	-2	22.39

28	0	0	0	2	51.72
29	0	0	0	0	38.64
30	0	0	0	0	37.97

$$\alpha = 2^{\frac{n}{4}}$$ (4)

where n is the number of design parameters. Considering that there are 4 design parameters in this study, therefore α is 2.

Polyacrylamide conversion (%) was used as the dependent response fitted by a second-order model in the form of quadratic polynomial equation:

$$\text{Conversion (\%)} = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1, \ i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon$$ (5)

The approximation for the true functional relationship between the acrylamide redox polymerization conversion (%) and the set of independent design parameters are determined where β_o is the offset term, β_i is the linear effect, β_{ii} is the squared effect, β_{ij} represents the interaction effect, x_i are the coded variables and ε represents error[18].

The response and its corresponding analysis on the variations were analyzed with Minitab 14 statistical software to determine the effects of the design parameters, their interactions as well as statistical parameters of the model. The effects of the independent design parameters on the response were illustrated by three-dimensional surface plots and the optimized redox polymerization condition was obtained from the plots. ANOVA was used to analyze the response and the empirical model was constructed based on the significant terms with $p<0.05$. The quality of fit of the model was expressed by least square technique. To determine the adequacy of the proposed model, a validation test involving diagnostic plot of predicted response versus experimental response was carried out.

Fourier Transform Infrared (FT-IR) spectra analysis

The presence of various chemical functional groups and their changes were monitored using Avatar 360 FT-IR spectrophotometer. Acrylamide and polyacrylamide were prepared into platlets using potassium bromide. The platlets were tested after completion of the blank spectrum scanning. The FT-IR spectrophotometer was operated with a resolution of 4 cm^{-1} and scanning range from 4000 to 400 cm^{-1}. The chemical functional groups of acrylamide and polyacrylamide were determined based on the wavenumbers obtained from the FT-IR spectra.

Molecular weight distribution determination

Molecular weight of the polyacrylamide was determined using Waters 2414 Gel Permeation Chromatography (GPC), a differential refractive index meter as a detector and a series of Waters Ultrahydrogel columns (Linear, 500 and 120). Water was used as the mobile phase, and polyethylene oxide standards were employed for calibration. The polyacrylamide sample was dissolved in deionized water at the concentration of 0.1 % by weight. The aqueous sample was filtered through a 0.45 μm syringe filter prior to being injected into the GPC system. A 20 μL of sample was injected into the system with a flow rate of 1.0 mL/min and the temperature of the columns was kept constant at 40°C in a column oven. The data collected was processed by Breeze software.

Intrinsic viscosity and solution viscosity measurement

Polyacrylamide solution was prepared by dissolving a known weight of polyacrylamide powder in deionized water as solvent. The polyacrylamide solution was agitated to ensure complete dissolution. For each concentration, the flow time of the solution was measured[4]. Specific viscosity of polyacrylamide solution was determined using an Ubbelohde viscometer in thermostatic water bath at 30°C. Intrinsic viscosity [η] of

polyacrylamide solution was obtained using a dilution extrapolation method as shown in Eq. 6, where water was used as the solvent. A linear regression was fitted to determine the intercept of the plot which it was the intrinsic viscosity value located.

$$[\eta] = \lim_{c \to o} \frac{\eta_{sp}}{C} \tag{6}$$

$$\eta_{sp} = \frac{t_1 - t_0}{t_0} \tag{7}$$

where $[\eta]$ = intrinsic viscosity, η_{sp} = specific viscosity, C = polyacrylamide solution concentration, t_1 = polyacrylamide solution flow time, t_0 = solvent flow time

The viscosity of the solution was determined by:

$$\eta = A\rho t \tag{8}$$

where η = solution viscosity, A = calibration constant of the viscometer, ρ = density of polyacrylamide solution, and t = flow time.

Transmission electron microscopy (TEM) viewing

Acrylamide and polyacrylamide solutions were analyzed using Philips CM12 Transmission Electron Microscope to visualize their molecular structure before and after redox polymerization. One drop of acrylamide or polyacrylamide solution were carefully placed on the copper grid and dried with filter paper under a clean environment to ensure there were no impurities that might interfere with the TEM viewing. The acrylamide and polyacrylamide solution-coated copper grids were then put under TEM for image viewing.

Results and Discussion

Optimization of the polyacrylamide redox polymerization

Four design parameters i.e., polymerization temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite were taken into account for redox polymerization optimization. Parameters screening was carried out using 2^4 full factorial design. Significant main parameters and interactive parameters were included for RSM analysis. Redox polymerization of polyacrylamide was optimized using CCD where 30 runs were required to cover all possible parameter levels combinations. The three-dimensional response surface plots showing significant effect on the polyacrylamide conversion (%) are given in Figure 1a to 1e All response surface plots show similar trend where the response increases with the levels of design parameters. Interactive effect of ammonium persulphate and temperature in Figure 1a shows the most significant effects where both ammonium persulphate concentration and temperature play vital roles in initiating polyacrylamide polymerization[19,20,21,22,23]. Persulphate associated initiation system required temperature elevation to initiate the polymerization whereby temperature 40°C to 70°C was the ideal temperature range in initiating polyacrylamide polymerization[19,20,21,22,23]. However, polyacrylamide conversion (%) was reported to be very low at temperature <45°C [22]. This is because the free persulphate radical production rate is dependent on the temperature. With the elevation of temperature, free persulphate radical is favourable in attacking acrylamide vinyl bond to form polyacrylamide. The interactions of acrylamide with sodium bisulfite and ammonium persulphate are shown in Figure 1b and 1c, respectively. With the increase of acrylamide feed concentration, more acrylamide are wrapped in the solvent-monomer solution[21]. Thus, more sodium bisulfite and ammonium persulphate are needed in the free radical reaction. According to Daughton, acrylamide is readily polymerized with elevated temperature[2]. This is proven in Figure 1d, where there is a drastic increase in the polyacrylamide conversion (%) with the increase in temperature. Hunkeler & Hamielec have compiled works using different kinds of redox initiator couples for polyacrylamide polymerization[24]. Redox initiation couple, typically consisting of persulphate-group and bisulfite group, has been proven to be effective in initiating polymerization[10]. Figure 1e shows the interaction between ammonium persulphate and sodium bisulfite in initiating polyacrylamide redox polymerization. The presence of bisulfite ion in the reaction helps in decomposing persulphate ions[11]. However, the relative strength of sodium bisulfite on polyacrylamide redox polymerization was weak compared to ammonium persulphate. This is because sodium bisufite used was controlled at relatively low concentration compared to ammonium persulphate considering excess of bisulfite ions used in the reaction could reduce the

degree of polymerization. When the bisulfite concentration is high; more sulfonate group will be produced (Pohl and Rodriguez, 1980):
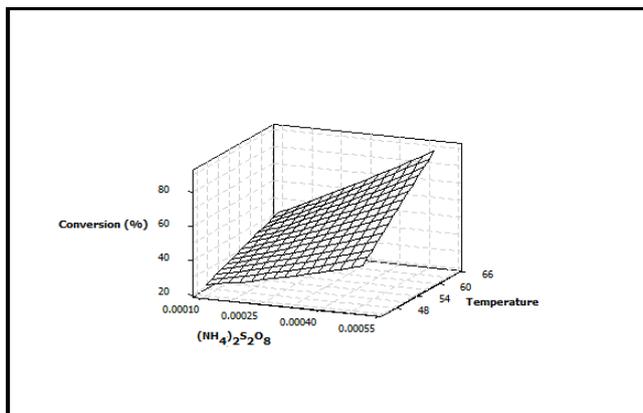

Figure 1a Response surface plot for the interactive effect of ammonium persulphate concentration and temperature on polyacrylamide conversion (%).
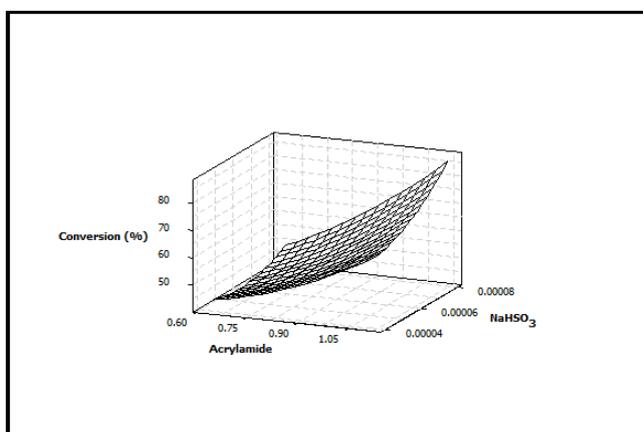

Figure 1b Response surface plot for the interactive effect of acrylamide and sodium bisulfite concentrations on polyacrylamide conversion (%).
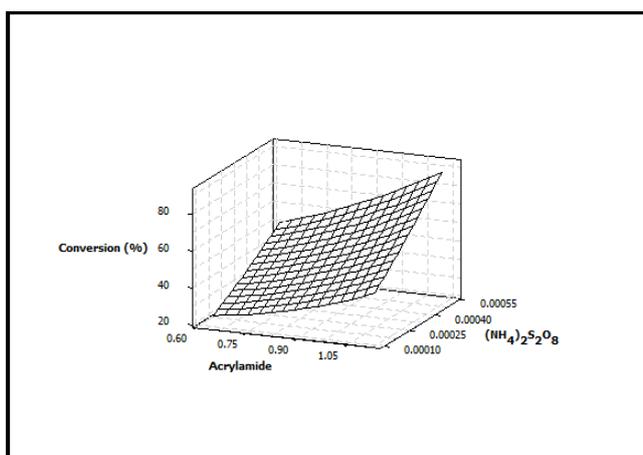

Figure 1c Response surface plot for the interactive effect of acrylamide and ammonium persulphate concentrations on polyacrylamide conversion (%).
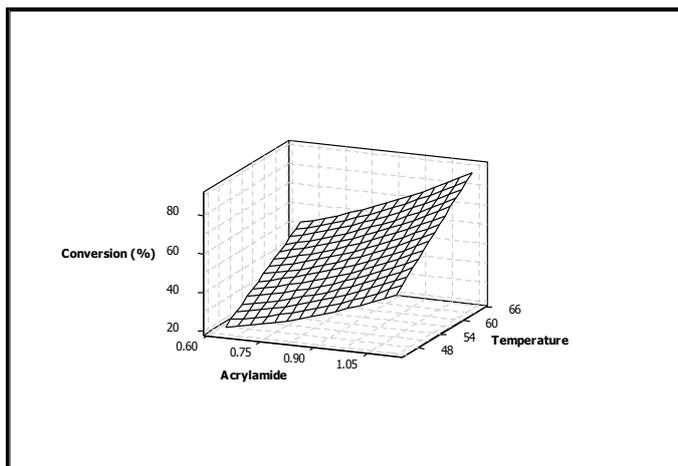
Figure 1d Response surface plot for the interactive effect of acrylamide concentration and temperature on polyacrylamide conversion (%).
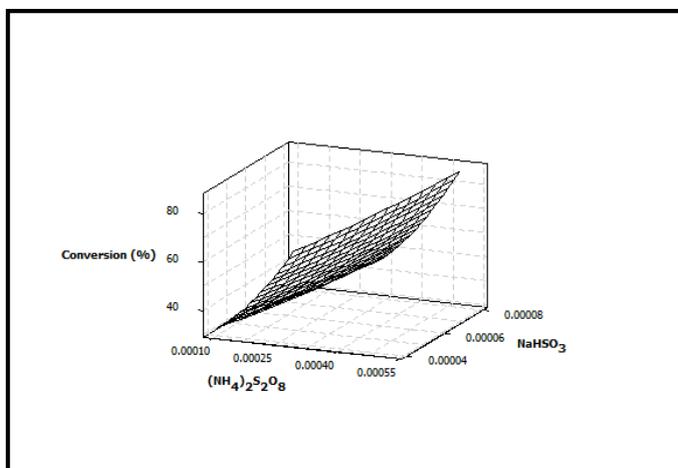

Figure 1e Response surface plot for the interactive effect of ammonium persulphate and sodium bisulfite concentrations on polyacrylamide conversion (%).

$$SO_4^- \cdot + HSO_3^- \rightarrow SO_4^{2-} + HSO_3 \cdot \qquad\qquad (9)$$

The sulfonate radicals tend to react with acrylamide and stop the polyacrylamide chain propagation:

$$CH_2CHCONH_2 \cdot + HSO_3^- \rightarrow CH_2CH_2CONH_2 + SO_3^- \qquad\qquad (10)$$

The highest polyacrylamide conversion (%) was achieved between high level and positive axial of temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite. The optimal redox polymerization condition, which produces the maximum polyacrylamide conversion (%), was obtained by using 1.0335M of acrylamide, 5×10^{-4} M of ammonium persulphate, 1×10^{-4} M of sodium bisulfite under 65°C. An experiment was carried out to validate the optimal redox polymerization condition; the maximum polyacrylamide conversion (%) was 96.89%. The result shows a high accuracy in obtaining polyacrylamide conversion (%) as expressed in normal probability plot of the standardized residuals in Figure 2. The checkpoints distributed closely along the straight line indicating normality for all responses.

Regression analysis

Using regression analysis, the polyacrylamide conversion (%) can be correlated with the four design parameters studied (temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite). A second-order model based on the estimated regression coefficients for respective coded design parameters is shown in Table 3. The regression model for polyacrylamide conversion (%) was constructed as follows:

Table 3 Estimated regression coefficients for acrylamide redox polymerization.

Term	Coef	SE Coef	T	P
Constant	38.7133	0.13417	288.548	0.000
x_1	5.8943	0.06626	88.957	0.000
x_2	7.0905	0.06626	107.011	0.000
x_3	2.6834	0.06626	40.498	0.000
x_4	7.1618	0.06626	108.087	0.000
x_1^2	0.7861	0.06198	12.683	0.000
x_2^2	0.2788	0.06198	4.498	0.000
x_3^2	0.8851	0.06198	14.281	0.000
x_4^2	-0.0662	0.06198	-1.068	0.289
x_1x_2	0.9399	0.08115	11.583	0.000
x_1x_3	0.9498	0.08115	11.704	0.000
x_1x_4	0.5675	0.08115	6.993	0.000
x_2x_3	0.2665	0.08115	3.284	0.002
x_2x_4	1.5672	0.08115	19.312	0.000
S = 0.5622	R-Sq = 99.8%		R-Sq(adj) = 99.7%	

$$\text{Conversion (\%)} = 38.7133 + 5.8943x_1 + 7.0905x_2 + 2.6834x_3 + 7.1618x_4 + 0.7861x_1^2 + 0.2788x_2^2 + 0.8851 x_3^2 + 0.9399x_1x_2 + 0.9498x_1x_3 + 0.5675x_1x_4 + 0.2665x_2x_3 + 1.5672x_2x_4 \tag{11}$$

where x_1 represents concentration of acrylamide, x_2 represents concentration of ammonium persulphate, x_3 represents concentration of sodium bisulfite and x_4 represents polymerization temperature. The coefficient with one design parameter represents the effect of the particular design parameter, while the coefficient with two design parameters and those with second-order terms represent the interaction between two design parameters, and quadratic effect, respectively. The positive sign indicates synergistic effect. The corresponding ANOVA table of the fitted model is shown in Table 4. The linear (x_1, x_2, x_3 and x_4), quadratic (x_1^2, x_2^2 and x_3^2) and interaction (x_1x_2, x_1x_3, x_1x_4, x_2x_3 and x_2x_4) terms were found to be significant at 95% confidence level. The ANOVA shows that the second-order model fits the experimental data adequately where the linear, quadratic and interaction terms of design parameters show significant effect on the polyacrylamide conversion (%), while the lack of fit was not significant (p>0.05) indicating the designed model fit the experimental data adequately[18].

Table 4 ANOVA table for acrylamide redox polymerization using central composite design.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	13	10663.5	10663.5	820.27	2594.93	0.000
Linear	4	10332.7	10332.7	2583.18	8171.89	0.000
Square	4	108.3	108.3	27.09	85.69	0.000
Interaction	5	222.5	222.5	44.49	140.75	0.000
Residual error	71	22.4	22.4	0.32		
Lack-of-fit	59	20.1	20.1	0.34	1.78	0.137
Pure error	12	2.3	2.3	0.19		
Total	89	10784.8				

Validation of the fitted model

It is necessary to conduct a model validation to ensure the fitness of the regression model. A diagnostic plot consisting of predicted conversion (%) versus experimental conversion (%) was plotted to determine the adequacy of the empirical model to the experimental data. The predicted conversion (%) versus experimental conversion (%) plot is shown in Figure 3 with the R^2 value of 0.9924. This shows that the regression model constructed is adequate to describe the response of the polyacrylamide redox polymerization.
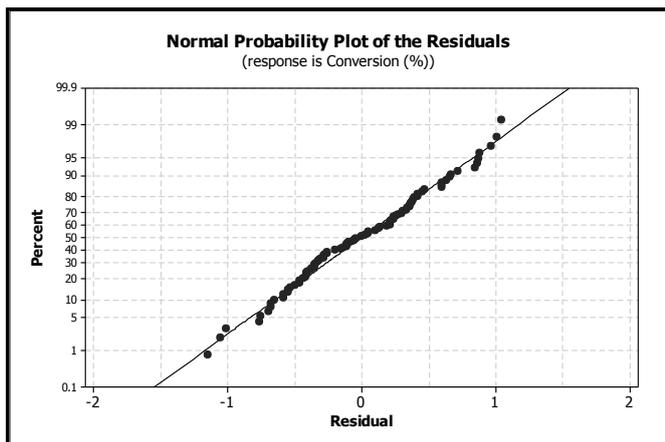
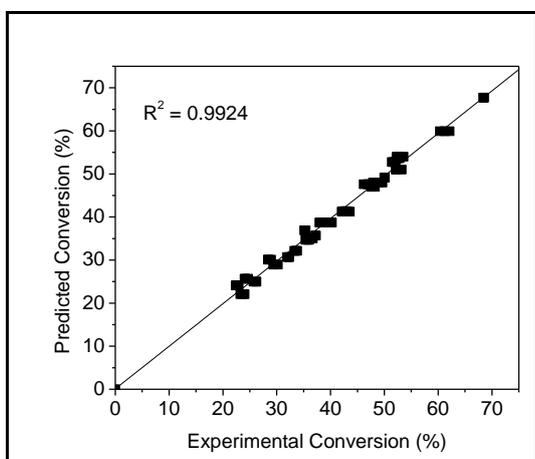**Figure 2 Normal probability plot of the standardized residuals.**

Figure 3 Predicted conversions (%) versus experimental conversion (%) for acrylamide redox polymerization.

Fourier transform infrared (FT-IR) spectra analysis of polyacrylamide

The FT-IR spectra of acrylamide and polyacrylamide are shown in Figure 4. The wavenumbers that indicates the presence of various chemical functional groups and their changes are given in Table 5. The chemical functional groups change with the conversion of acrylamide to polyacrylamide is confirmed by IR spectrum. In acrylamide spectra, 3382.46, 1673.60 and 1352.26 cm^{-1} assigned as amides primary $-CONH_2$ for NH stretch, C=O stretch (amide I) and C-N stretch (amide III) respectively. Primary amines was identified in 2813.12 and 1613.75 cm^{-1} for CH stretch and NH_2 deformation, respectively. In comparison with acrylamide, vinyl CH_2=CH- (CH deformation) in 988.96 and 961.28 cm^{-1} has disappeared; new alkyl R- (CH stretch and CH_2 deformation) spectra were found in 2932.56 and 1455.48 cm^{-1} of polyacrylamide. Absence of the vinyl spectra in the IR spectrum of polyacrylamide [-CH_2-CH($CONH_2$)-]$_n$ indicates that the vinyl group has been transformed into saturated carbon chain during redox polymerization. Primary amides $-CONH_2$ and primary amines in polyacrylamide spectra were characterized for NH stretch and NH_2 deformation in 3477.32 and 1646.84 cm^{-1}, respectively. For bands between 1300 – 500 cm^{-1} for polyacrylamide, no significant peak was detected. With the elucidation of FT-IR spectra, the conversion of acrylamide to polyacrylamide has been confirmed.

Table 5 Observed FT-IR wavenumbers and their corresponding functional group and assignments for acrylamide and polyacrylamide.

Acrylamide			Polyacrylamide		
Wavenumber (cm^{-1})	**Group or Class**	**Assignment and Remarks**	**Wavenumber (cm^{-1})**	**Group or Class**	**Assignment and Remarks**
3382.46 (m)	Amides primary -CONH$_2$	NH stretch	3477.32 (m)	Amides primary -CONH$_2$	NH stretch

			2932.56 (m)	Alkyl R-	CH stretch
2813.12 (m)	Amines primary	CH stretch			
1673.60 (vs)	Amides primary -CONH$_2$	C=O stretch (amide I)			
1613.75(s)	Amines primary	NH$_2$ deformation	1646.84 (s)	Amines primary	NH$_2$ deformation
			1455.48 (m)	Alkyl R-	CH$_2$ deformation
1429.19 (vs)	-CH$_2$-	CH$_2$ deformation			
1352.26 (m-s)	Amides primary -CONH$_2$	C-N stretch (amide III)			
988.96 (s)	Vinyl CH$_2$=CH-	CH deformation			
961.28 (s)	Vinyl CH$_2$=CH-	CH deformation			

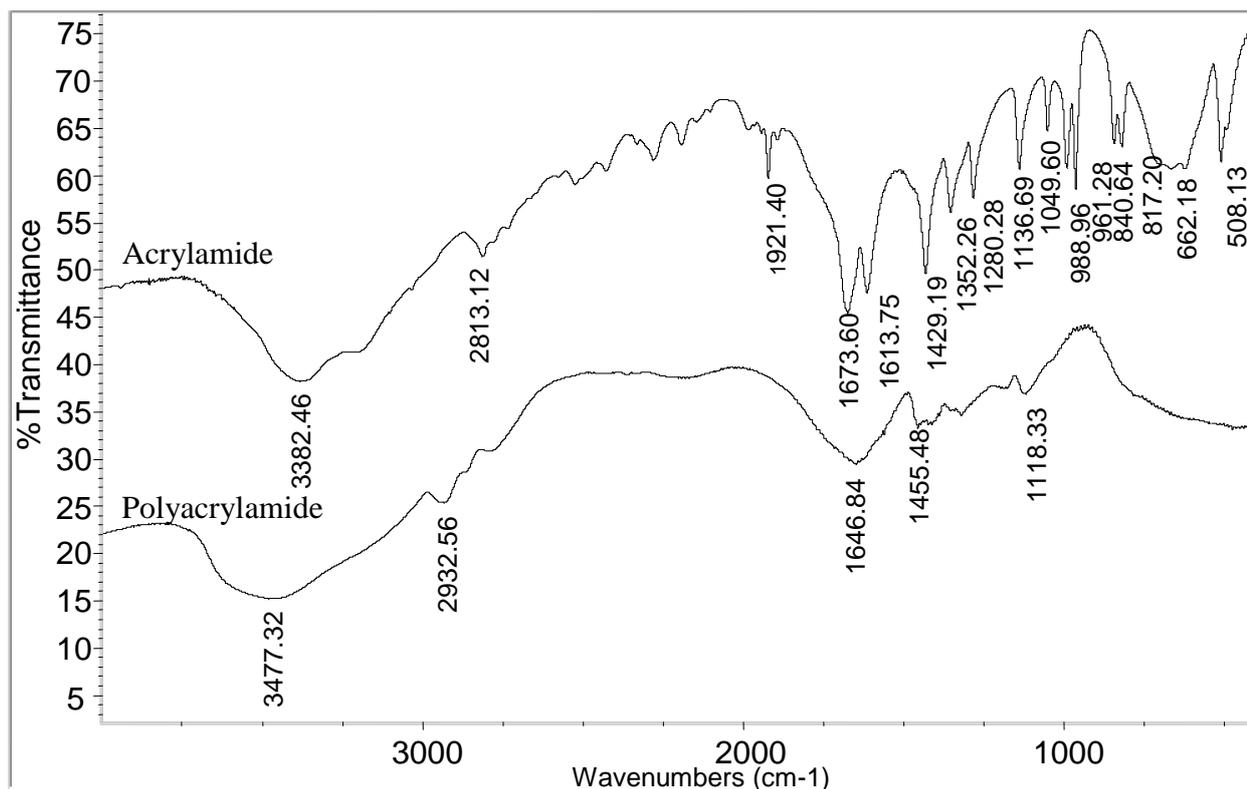*vs = very strong, s = strong, m = medium

Figure 4 FT-IR spectra for acrylamide and polyacrylamide.

Molecular weight distribution

Gel Permeation Chromatography (GPC) which employs a physical separation of molecules, provides a better indicator of the molecular weight dynamics by providing the distribution of molecular weights[25]. Molecular weight distributions obtained from a sample are always based on cumulative distributions[26]. The molecular weight distribution of polyacrylamide in cumulative form is shown in Figure 5. The optimized polyacrylamide molecular weight is distributed along the range of 1.45 x 10^5 to 3.40 x10^6 Da and it has a peak molecular weight of 2.02 x 10^6 Da. Based on the Table 6, the weight average molecular weight (Mw) of the optimized polyacrylamide is 1.66 x 10^6 Da with the polydispersity of 1.3555.

Table 6 Molecular weight distribution of polyacrylamide.

	Mn (Da)	Mw (Da)	Mz (Da)	Polydispersity
Polyacrylamide	1.22×10^6	1.66×10^6	2.00×10^6	1.3555

Mn : the number average molecular weight
Mw: the weight average molecular weight
Mz: the size average molecular weight

Intrinsic viscosity and viscosity of polyacrylamide aqueous solution

The intrinsic viscosity of polyacrylamide aqueous solution was determined from the extrapolation of the specific viscosity at zero concentration as shown in Figure 6. The y-intercept at 246 mL/g represents the intrinsic viscosity value for the optimized polyacrylamide. The viscosities of the polyacrylamide aqueous solution were determined. Figure 7 shows the viscosities of the polyacrylamide aqueous solution at different concentrations. Viscosity increases from 4.34 mPa.s to 15.37 mPa.s with the increase of polyacrylamide concentration from 3.33×10^{-3} to 7.14×10^{-3} g/mL. The viscosity changes at a different rate depending on the polyacrylamide concentrations where this observation can be explained in three distinctive features:
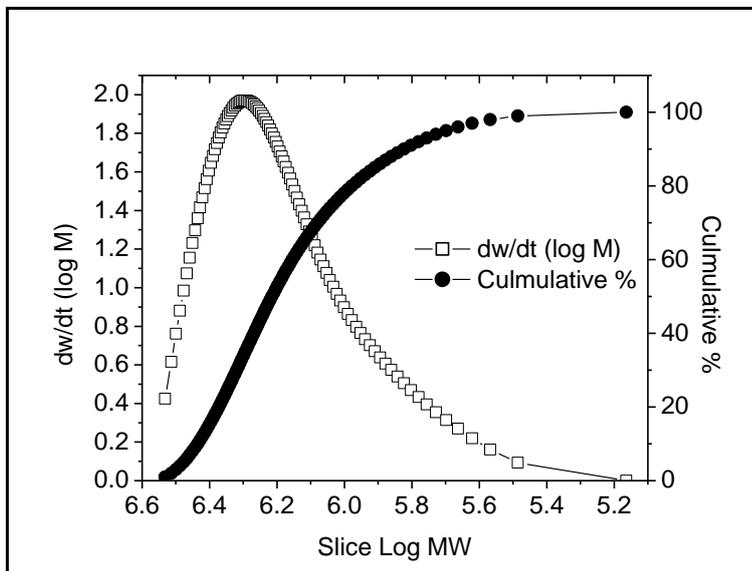

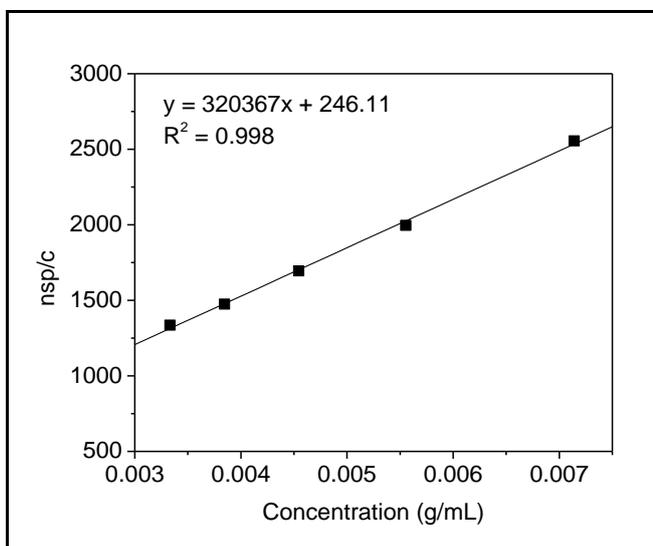**Figure 5 Molecular weight distribution of polyacrylamide.**

Figure 6 Plot of specific viscosity/concentration versus concentration for optimized polyacrylamide.
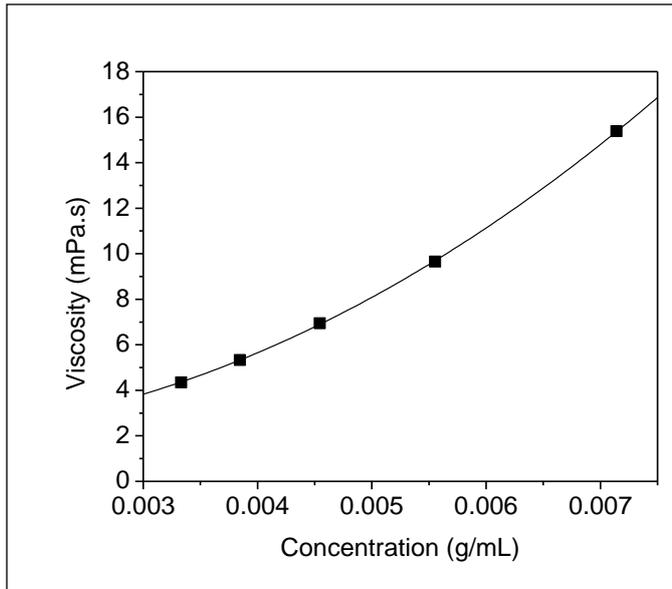
Figure 7 The solution viscosity of polyacrylamide at different concentrations.

(i) At low polyacrylamide concentration, the polyacrylamide chains have little chance to interact with each other. Polyacrylamide chains are expanded by the excluded volume effect at low concentration. The changes of viscosity over concentrations are observed to be relatively low.

(ii) At moderate polyacrylamide concentration, polyacrylamide begins to interact between each other and the viscosity starts to rise. This can be explained that polyacrylamide chains start to overlap at critical concentration C*as follows:

$$C^* = \frac{1}{[\eta]}$$ (12)

where C* is inversely proportional to the intrinsic viscosity [η], which represents the chain dimension or the segment density of the chain coil in solutions; namely, the higher the [η] of polyacrylamide solution, the larger the chain dimension and the lower critical concentration C* [25]. The critical concentration C* estimated was at 0.004 g/mL, which is in agreement with our results where the polyacrylamide solution viscosity started to increase drastically after 0.004 g/mL of polyacrylamide concentration. The chains start to contract with the increase of polyacrylamide concentration as the excluded volume repulsion between segments in the same chain becomes screened by segments of neighbouring chains.

(iii) At high polyacrylamide concentration, the intermolecular association has come into effect within the polyacrylamide chains and leads to entanglement of chains. The intermolecular association thus gives a rise to a network structure of polymer chains by approaching each other, leading to the drastic increase of solution viscosity[27,28].

Transmission electron microscopy (TEM)

As the polymerization process proceeded, the initiated acrylamide free radicals formed a saturated carbon-carbon bonding between each other to form polyacrylamide. Figure 8 shows the polyacrylamide structure under magnification power of 52,000x. Polyacrylamide was observed in linear tree-roots like structure. This linear tree-root like structure is favorable in bridging solid particles[5,26].
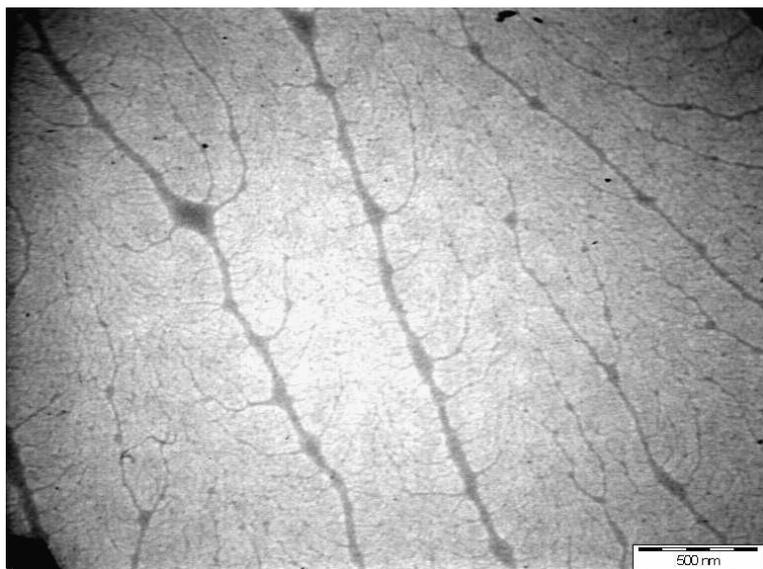
Figure 8 TEM image of polyacrylamide solution under magnification power 52,000x.

Conclusion

Response surface methodology has been used to optimize redox polymerization of polyacrylamide as a function of temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite. The optimum redox polymerization condition of 1.0335M acrylamide, 5×10^{-4} M ammonium persulphate and 1×10^{-4} M sodium bisulfite at 65°C was able to produce polyacrylamide conversion of 96.89% with molecular weight of 1.66×10^{6} Da in 10 minutes. A regression model has been constructed based on the empirical coefficients using related significant terms. FT-IR, GPC and TEM analysis were used to investigate the changes of chemical functional groups and molecular structure during the process of acrylamide conversion to polyacrylamide. The molecular structure was found to be a linear tree-roots structure under TEM viewing. The polyacrylamide produced can be applied in wastewater treatment whereby polyacrylamide works as a bridging agent to bind the suspended particles in wastewater to form larger flocs which to be removed through sedimentation.

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