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Process analysis and optimization for the ionic interactions of quaternary ammonium salts with nylon 66 fibers using statistical experimental design

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Abstract

A 2^4 response surface central composite design was successfully formulated using statistical software to establish the optimum process conditions for developing durable antimicrobial nylon 66 fibers through interactions with two different types of quaternary ammonium salts (QASs) namely cetylpyridinium chloride (CPC) and benzyldimethylhexadecyl ammonium chloride (BDHAC). The treatment conditions such as pH, temperature, concentration and time were studied for % exhaustion and thoroughly analyzed by analysis of variance (ANOVA) statistical concept. Appropriate predictable empirical models were developed incorporating interaction effects of all variables and then optimized. The significance of the mathematical model developed was ascertained using Microsoft Excel regression (solver) analysis module. The theoretical optimum conditions for 100% exhaustion were found to be pH 10.83, temperature 79 °C, concentration 1.63% omf and time 57 min for CPC and those for BDHAC were 10.75, 85 °C, 1.85% omf and 77 min, respectively. However, at the optimum conditions, maximum % exhaustion of 97.32% for CPC and 94.56% for BDHAC was achieved experimentally.

Keywords: Optimization; Nylon fibers; Quaternary ammonium salts; % Exhaustion; Statistical experimental design

1. Introduction

The production of textile fibers is a global industry and the end-uses for textile-based materials continue to expand every year as the unique properties of textile fibers are utilized in many industries. So, in recent days, many studies for improving the qualities as well as incorporating new functional groups into the fibers are being carried out by means of chemical or physical modifications. Durable wrinkle-free cotton [1,2], durable fire resistant cotton [3,4], durable antimicrobial cottons [5,6], antimicrobial wool [7] are examples of the chemical modifications of fibers. Acrylic fibers become dyeable by incorporating a co-monomer containing sulfonate or carboxylate groups that are interactive with cationic dyes [8]. Shrink proof wool was developed by acid chlorination of the wool or by the application of permonosulfuric acid (PMS), followed by a biopolymer application [9]. Electron beam modification was done on cotton, cotton/polyester film and nylon 6 by coating with polyvinyl alcohol (PVA) and acrylic acid [10]. Coloration of nylon fabrics with acid dyes was carried out using the ionic interactions between protonated amino end groups of the polyamides and sulfonate or carboxylic acid groups of the dyes [11]. By incorporating the halamine structures [12,13] and also by the addition of the reactive agents [14] that are interactive with the incorporated acid dyes, attempts were previously made to develop antimicrobial nylon fibers.

With similar approach, a durable antimicrobial nylon 66 fiber was successfully developed through ionic interaction of cationic antimicrobial functional agents with the carboxylic end groups of the nylon 66 by the author [15]. Quaternary ammonium salt (QAS) is widely accepted as a strong

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antimicrobial agent as it contains a positively charged nitrogen atom in its chemical structure as shown in Fig. 1. The quaternary ammonium salts (QASs) were used as cationic antimicrobial functional agents which impart strong antimicrobial property and the effects of four process variables namely pH, temperature, QAS concentration and finishing time were studied in detail [15]. But, the traditional methods of experimentation were followed to study the effects of all variables which are lengthy, random processes and also require large number of experimental combinations to obtain the desired results. In addition, obtaining the optimum conditions i.e., the point at which maximum % exhaustion could be achieved, is almost beyond the scope.

The traditional step-by-step approach, although widely used, involves a large number of independent runs and does not enable us to establish the multiple interacting parameters. This method is also time consuming, material consuming and requires large number of experimental trials to find out the effects, which are unreliable. So, specifically designed experiments to optimize the system with lesser number of experiments are the need of the hour. These limitations of the traditional method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) [16]. So, in this research article, experiments were designed by incorporating all important process variables namely pH, temperature, concentration and finishing time using Statistical Design Software i.e., MINITAB 14 (PA, USA). Experimental design allows a large number of factors to be screened simultaneously to determine which of them has a significant effect on % exhaustion. A polynomial regression response model shows the relationship of each factor towards the response as well as the interactions among the factors. Those factors can be optimized to give the maximum response (% exhaustion) with a relatively lower number of experiments. In this context, a new approach using statistically designed experiments for developing durable antimicrobial nylon 66 fibers through interactions with two different types of quaternary ammonium salts (QASs) namely cetylpyridinium chloride (CPC) and benzyldimethylhexadecyl ammonium chloride (BDHAC) was discussed in detail. The corresponding interactions among the variables were studied and optimized using response surface methodology.

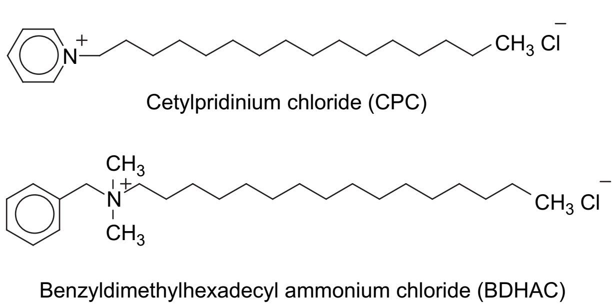

Fig. 1. Molecular structure of quaternary ammonium salts.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical grade and doubly distilled water was always used. Nylon 66 was purchased from Korea Apparel Testing and Research Institute (KATRI).

The two different quaternary ammonium salts CPC and BDHAC were purchased from Aldrich Chemical Co.

2.2. Apparatus

A Hewlett Packard UV–vis spectrophotometer, model HP8452 was used for measuring the absorbance and recording the normal and derivative spectra. A Corning model 220 pH meter was used for pH measurements.

2.3. Factorial experimental design and optimization of the variables

Temperature, pH, concentration and finishing time were chosen as independent variables and the % exhaustion as dependent output response variable. Independent variables, experimental ranges and levels for CPC and BDHAC are given in Table 1. The formulated design matrix, shown in Table 2, is a response surface central composite design consisting of 31 sets of coded conditions. It comprises a full replication of 2^4 (=16) factorial design plus seven center points and eight star points. All the variables at the intermediate level (0) constitute the center points and the combinations of each of the variables at either its lowest (−1) level or highest (−1) level with the other three variables at the intermediate levels constitute the star points. Thus, 31 experimental runs allowed the estimation of the linear, quadratic and two-way interactive effects of the process variables on the % exhaustion. Experimental plan showing the coded value of the variables together with % exhaustion of both CPC and BDHAC is given in Table 2. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (1)$$

The results of the experimental design were studied and interpreted by MINITAB 14 (PA, USA) statistical

Table 1
Experimental ranges and levels of process variables for % exhaustion of CPC and BDHAC onto nylon 66

Independent variables	Range and level				
	$-\alpha$	−1	0	1	$+\alpha$
pH (X_1)	9	10	11	12	13
Temperature (°C, X_2)	41	60	80	100	117
Concentration (%omf, X_3)	2.25	0.5	3.25	6	8.75
Time (min, X_4)	15	10	35	60	85

Table 2
Response surface central composite design matrix for % exhaustion of CPC and BDHAC onto nylon 66

S.no.	pH	Temperature	Concentration	Time	% Exhaustion			
					CPC		BDHAC	
					Exp.	Pred.	Exp.	Pred.
1	−1	−1	−1	−1	73.16	73.32	64.82	64.76
2	1	−1	−1	−1	69.04	68.93	59.25	61.22
3	−1	1	−1	−1	80.41	80.44	72.65	71.22
4	1	1	−1	−1	78.44	78.43	69.85	69.81
5	−1	−1	1	−1	53.20	53.24	43.85	43.43
6	1	−1	1	−1	40.79	40.76	31.25	29.40
7	−1	1	1	−1	65.88	65.83	55.35	58.09
8	1	1	1	−1	55.615	55.73	46.45	46.19
9	−1	−1	−1	1	90.42	90.55	83.47	83.07
10	1	−1	−1	1	76.79	76.73	75.65	73.07
11	−1	1	−1	1	94.62	94.61	90.32	92.33
12	1	1	−1	1	91.15	91.18	84.64	84.45
13	−1	−1	1	1	54.86	54.89	45.85	46.19
14	1	−1	1	1	32.95	32.98	24.98	25.70
15	−1	1	1	1	72.49	72.42	66.47	63.63
16	1	1	1	1	52.72	52.90	44.87	45.27
17	−α	0	0	0	66.78	67.19	57.45	57.62
18	α	0	0	0	42.89	43.27	34.65	35.72
19	0	−α	0	0	55.40	55.33	46.65	47.50
20	0	α	0	0	82.43	82.36	73.98	73.54
21	0	0	−α	0	89.58	89.48	79.55	80.63
22	0	0	α	0	38.01	37.91	29.55	29.98
23	0	0	0	−α	81.48	81.37	73.65	71.58
24	0	0	0	α	88.86	88.76	79.95	80.73
25	0	0	0	0	84.87	84.76	75.65	75.64
26	0	0	0	0	84.87	84.76	75.65	75.64
27	0	0	0	0	84.87	84.76	75.65	75.64
28	0	0	0	0	84.87	84.76	75.65	75.64
29	0	0	0	0	84.87	84.76	75.65	75.64
30	0	0	0	0	84.87	84.76	75.65	75.64
31	0	0	0	0	84.87	84.76	75.65	75.64

software to estimate the response of the dependent variable (% exhaustion).

2.4. Nylon 66 fiber treatment

Nylon fibers (warp 70f24, weft 140f48, 2 g) were treated with CPC and BDHAC separately in sealed, stainless steel dye pots of 120 cm^3 capacities in a laboratory-scale infrared dyeing machine (ACE-6000T). Experiments were performed according to response surface central composite design given in Table 2. The pH was adjusted using 0.1 N Na_2CO_3 and 0.1 N CH_3COOH. At the end of treatment, the nylon 66 sample was removed, rinsed thoroughly in tap water and dried in open air. The exhaustion rate (%E) was then calculated using the formula,

$$\%\ \text{Exhaustion} = \left[\frac{D_0 - D_t}{D_0}\right] \times 100 \quad (2)$$

where D_0 and D_t are the quantities of QAS in the initial and final bath, respectively. Those values were calibrated through absorbance measurement of original and exhausted bath by UV−vis spectrophotometer.

2.5. Empirical modeling

Empirical model i.e., second-order polynomial regression equations were developed using Excel solver function to predict the % exhaustion, relating the process variables i.e., pH, temperature, concentration and time. RMSE (root mean square error) is the important tool to validate the model equation for its prediction capacity [17]. The RMSE is the distance, on average, of a data point from the fitted line, measured along a vertical line. If the value of RMSE is zero, then the model is said to be perfectly predicting the behaviour of the system i.e., ideal model. The prediction capacity of the model thus decreases with respect to the corresponding value of the RMSE from zero. So, series of the equations varying the combinations of the variables like interaction effects and squared effects were run using solver function so as to get the least value of the RMSE. The goodness of fit is a measure of how well the model fits the data. Model is only developed with a sample, and the value of the model depends on the clarity and unambiguity of the relationships between the independent variables.

The behaviour of the system was explained by the following empirical model [17]:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i^2 + \sum \beta_{ij} x_i x_j \quad (3)$$

where Y is the dependent variable, β is the regression coefficient, and x is the independent data. Root mean square error (RMSE) was calculated using the following formula [17]:

$$\text{RMSE} = \sqrt{\frac{\sum_0^N (\text{Exp.} - \text{Pred.})^2}{N}} \quad (4)$$

where Exp. is the experimental value, Pred. is the predicted value from model equations and N is the total number of experiments.

2.6. Data analysis

MINITAB 14 (PA, USA) was used for the statistical analysis of the experimental data obtained. The quality of fit of the polynomial model equation was expressed by the coefficient of determination R^2 and its statistical significance analyzed by Fisher's F-test and Student's t-test (analysis of variance (ANOVA)). The level of significance was given as values of P less than 0.0001. A differential calculation (Monte-Carlo optimization) was then employed for predicting the optimum point.

3. Results and discussion

The most important variables which affect the % exhaustion of the QAS onto nylon 66 fibers are pH, temperature, concentration and finishing time. In order to study the combined effect of these factors, experiments were performed at different combinations of the physical variables using statistically designed experiments. The pH range studied was between 9 and 13, temperature was between 41 °C and 117 °C, concentration was between 2.25% omf and 8.75% omf and finishing time was between 15 min and 85 min. The experiments were carried out according to the response surface central composite design matrix given in Table 2. The samples were analyzed for % exhaustion using UV spectrophotometer.

The main effects of each of the variables on % exhaustion are given in Figs. 2 and 3 for CPC and BDHAC, respectively, and similar graphs were obtained for both the salts. From Figs. 2 and 3, it was observed that the maximum % exhaustion was found to be pH 11 for both CPC and BDHAC. This indicates the fact that alkaline pH will be the ideal reaction condition for nylon 66 fibers with both the cationic compounds i.e., CPC and BDHAC. Polyamides have two different end groups such as amino and carboxylate groups. Both groups are chemically active and the amino end groups have been widely employed in the acid dyeing of nylon under acidic condition. But, carboxylic acid ends have rarely been utilized in either dyeing or chemical finishing of the polyamide substrates [15]. Carboxylic acid groups will become more attractive with cationic groups under basic conditions at which these groups can form carboxylate anions (Fig. 4).

The pH 11 leads to a higher exhaustion since the cationic quaternary ammonium salts are more attractive to the negatively charged carboxylate groups under the basic condition. Due to ionic interactions, cationic salts were quickly adsorbed and diffused into fibers. The increased exhaustion could lead to increased diffusion of the salts into the substrates. The higher exhaustion of the QASs are expected in better antimicrobial functions on the QAS treated fibers. But, at the pH above 11, decrease in exhaustion was observed as the polyamides have limited carboxylic end groups, and hence excess alkaline condition which is more than what actually can ionize the nylon polymer, plays a negative role in decreasing the % exhaustion.

Higher temperature (>60 °C) was found to be better for maximum % exhaustion for both CPC and BDHAC and % exhaustion decreased with decrease in temperature. Above the glass transition temperature (>60 °C), the amorphous regions of polyamide will provide more free volume to diffuse more QAS and as a result, higher exhaustion of QAS occurs. In addition, a swelling effect resulted from the higher temperature and alkaline conditions should facilitate diffusion of QAS into nylon polymer. The size of the QAS plays an important role in the difference of exhaustion. The larger molecular size reduces the strength of the interactions between the ions and the diffusion velocity of the bulky salt and hence bulky BDHAC showed lower exhaustion compared to small CPC compounds at the same experimental condition.

Diffusion of QAS into nylon polymer depends on the concentration of salts of the finishing bath. The concentration of QAS directly affects the uptake rates of salts on nylon polymer due to ionic interactions between the carboxylate groups and QAS. From the main effects plot (Figs. 2 and 3) for both CPC and BDHAC, it was observed that lower concentration resulted in higher % exhaustion while increase in concentration resulted in decrease in % exhaustion. Maximum % exhaustion was achieved at the concentration of 2.25% omf for both the salts. This may be attributed to the fact that polyamides have limited carboxylic end groups and an excess amount of QAS in the finishing bath that could not produce a higher exhaustion than the maximum amount of the end groups and instead play a negative role in decreasing the exhaustion of QAS onto nylon.

Usually, the QAS can only enter into amorphous regions in the polymer by diffusion, while nylon 66 fibers contain about 30% of the amorphous areas and 70% of the crystalline

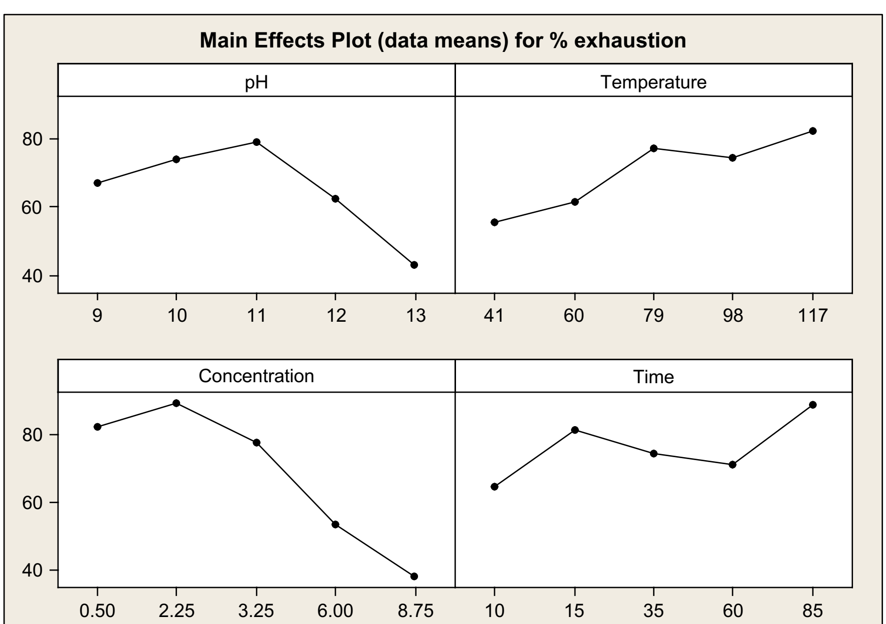

Fig. 2. Main effects plot of variables on % exhaustion of CPC onto nylon 66 fibers.

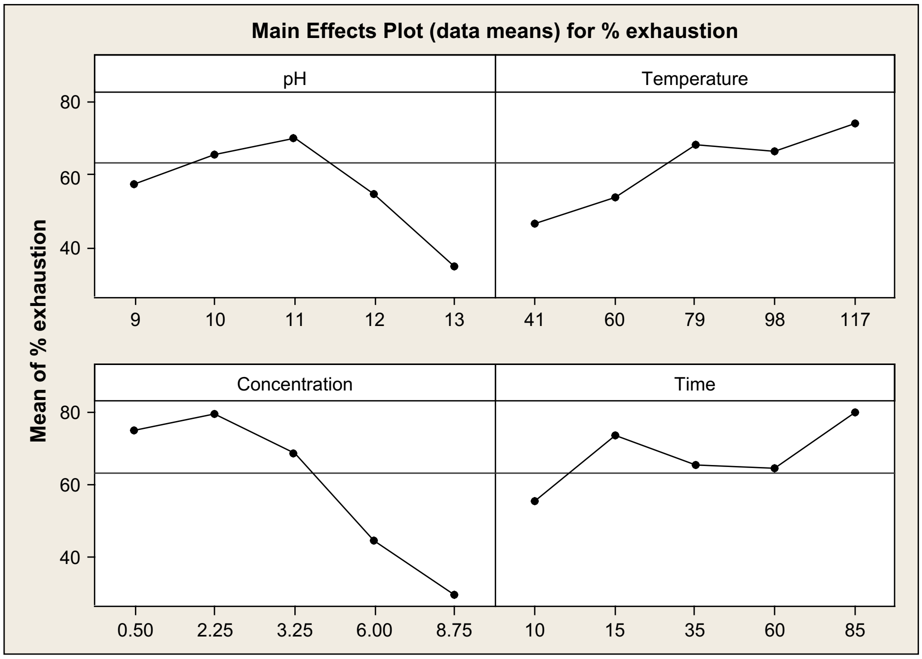

Fig. 3. Main effects plot of variables on % exhaustion of BDHAC onto nylon 66 fibers.

structure. The majority of the polymer structure is crystalline, which is tightly packed and difficult to penetrate for QAS. So, finishing time is quite important to the exhaustion of the QAS onto nylon. From the main effects plot, it is observed that higher treatment time (85 min) leads to higher exhaustion of the QAS. This indicates that higher the contact time between QAS and nylon polymer, higher the diffusion of QAS into the nylon polymer and hence, higher the exhaustion.

Using the experimental results, the regression model equations (second-order polynomial) relating the % exhaustion and process variables were developed and are given in Eqs. (5) and (6). Polynomial regression equation for % exhaustion of CPC onto nylon 66:

$$\begin{aligned} Y = & -862.9203+(159.6317X_1)+(1.5452X_2)+(6.5007X_3) \\ & +(1.2408X_4)-(7.3816X_1X_1)-(0.0110X_2X_2) \\ & -(0.5839X_3X_3)-(0.0012X_4X_4)+(0.03134X_1X_2) \\ & -(0.7357X_1X_3)-(0.0942X_1X_4)-(0.0261X_2X_3) \\ & +(0.0026X_2X_4)-0.0566(X_3X_4) \end{aligned} \quad (5)$$

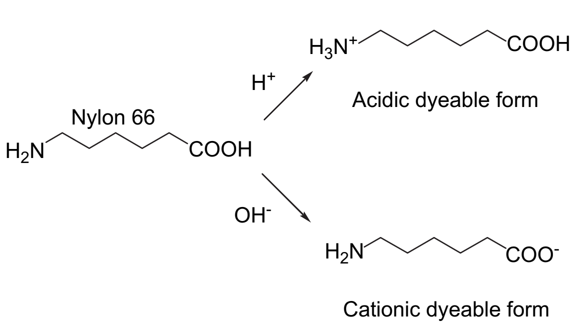

Fig. 4. Dissociation scheme of nylon 66 at acidic and alkaline conditions.

Polynomial regression equation for % exhaustion of BDHAC onto nylon 66

$$\begin{aligned} Y = & -855.07928+(156.9943X_1)+(1.5100X_2)+(7.1706X_3) \\ & +(1.0530X_4)-(7.2419X_1X_1)-(0.0104X_2X_2) \\ & -(0.5092X_3X_3)-(0.0014X_4X_4)+(0.0279X_1X_2) \\ & -(0.9528X_1X_3)-(0.0045X_1X_4)+(0.03923X_2X_3) \\ & +(0.0014X_2X_4)-0.0565(X_3X_4) \end{aligned} \quad (6)$$

where $X_1 = \text{pH}$, $X_2 = \text{temperature}$, $X_3 = \text{concentration}$, $X_4 = \text{time}$ and $Y = \%$ exhaustion.

Apart from the linear effect of the variables for the exhaustion, the RSM also gives an insight into quadratic and interaction effects of the variables. These analyses were done by

Table 3
Estimated regression coefficients and corresponding *t*- and *P*-values for CPC

Term	Coefficients	SE coefficients	*t*	*P*
Constant	−862.9203	26.9876	−31.946	0.000
X_1	159.6317	4.3735	36.594	0.000
X_2	1.5452	0.1729	8.460	0.000
X_3	6.5007	1.1213	7.128	0.000
X_4	1.2408	0.1259	9.185	0.000
X_1X_1	−7.3816	0.1913	−38.761	0.000
X_2X_2	−0.0110	0.0005	−20.372	0.000
X_3X_3	−0.5839	0.0253	−27.059	0.000
X_4X_4	−0.0012	0.0004	−2.053	0.057
X_1X_2	0.03134	0.0135	2.819	0.012
X_1X_3	−0.7357	0.0934	−8.796	0.000
X_1X_4	−0.0942	0.0103	−8.518	0.000
X_2X_3	0.0261	0.0049	6.003	0.000
X_2X_4	0.0026	0.0005	4.087	0.001
X_3X_4	−0.0566	0.0037	−14.447	0.000

Table 4
Estimated regression coefficients and corresponding *t*- and *P*-values for BDHAC

Term	Coefficients	SE coefficients	*t*	*P*
Constant	−855.07928	43.7518	−19.890	0.000
X_1	156.9943	7.0984	22.480	0.000
X_2	1.5100	0.2810	5.487	0.000
X_3	7.1706	1.8525	3.884	0.001
X_4	1.0530	0.2051	5.166	0.000
X_1X_1	−7.2419	0.3105	−23.611	0.000
X_2X_2	−0.0104	0.0009	−12.186	0.000
X_3X_3	−0.5092	0.0555	−9.169	0.000
X_4X_4	−0.0014	0.0007	−2.136	0.048
X_1X_2	0.0279	0.0220	1.178	0.256
X_1X_3	−0.9528	0.1520	−6.298	0.000
X_1X_4	−0.0045	0.0167	−3.902	0.001
X_2X_3	0.03923	0.0080	4.925	0.000
X_2X_4	0.0014	0.0090	1.618	0.113
X_3X_4	−0.0565	0.0061	−9.306	0.000

means of Fisher's *F*-test and Student's *t*-test. The Student's *t*-test was used to determine the significance of the regression coefficients of the variables. The *P*-values were used as a tool to check the significance of the variables, which in turn may indicate the patterns of the interactions among the variables. In general, larger the magnitude of *t* and smaller the value of *P*, more significant is the corresponding coefficient [16]. The regression coefficient, *t*- and *P*-values for all linear, quadratic and interaction effects of the variables are given in Tables 3 and 4 for CPC and BDHAC, respectively.

The predicted values (using model equations) were compared with experimental results for both CPC and BDHAC and the data are shown in Table 2 and are also graphically represented in Fig. 5. It was observed that the coefficients for the linear effect of all the four variables pH, temperature, concentration and time ($P = 0$) were highly significant for both the salts except the concentration for BDHAC which has *P*-value of 0.001 and that can be considered as the least significant. The coefficients for the quadratic effect of pH, temperature and time ($P = 0$) were highly significant for both the salts. But, the variable, time could be considered as least significant

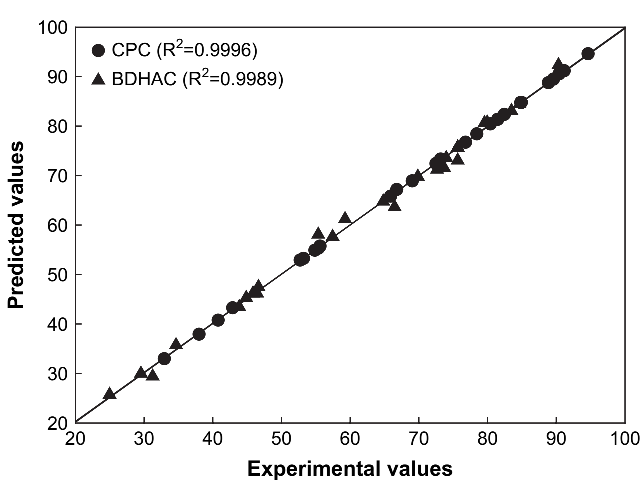

Fig. 5. Experimental and predicted values of % exhaustion of CPC and BDHAC.

for which *P*-value was 0.057 and 0.048 for CPC and BDHAC, respectively. All the four interaction effects were highly significant for both the salts except pH and temperature ($P = 0.012$ for CPC; $P = 0.256$ for BDHAC), temperature and time ($P = 0.001$ for CPC; $P = 0.113$ for BDHAC) could be considered as least significant. The significance of this quadratic and squared effects among the variables would have been lost if the experiments were performed by conventional or traditional approach.

Although few studies on the effects of variables on % exhaustion of nylon polymer have been reported in the literature, no attempt has been made to optimize them using statistical optimization methods. But, in this work, the model Eqs. (5) and (6) were optimized using multistage Monte-Carlo optimization technique [18]. The optimum values of the process variables were first obtained in coded units and then converted to uncoded i.e., real units by using Eq. (1). The optimum values of the process variables for the maximum % exhaustion are shown in Table 5. These results closely agree with those obtained by the response surface analysis i.e., graphically by contour and surface plots, confirming that the RSM could be effectively used to optimize the process variables in complex processes using the statistical design of experiments.

The contour and surface plots are model dependent and are useful for establishing desirable response values and operating conditions. In a contour plot, the response surface is viewed as a two-dimensional plane where all points that have the same response are connected to produce contour lines of constant responses. A surface plot displays a three-dimensional view that may provide a clear picture of the response surface. The stationary point or central point in the contour plot is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour levels in each of these figures will correspond to the optimum values of the respective constituents. The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram [19].

The contour plots given in Figs. 6 and 7 show the relative effects of any two variables when the remaining variables are kept constant. The contour plot for CPC in Fig. 6 shows the interactive effect of pH and concentration by maintaining time and temperature constant. Similarly by keeping time and temperature constant, the contour plot (Fig. 7) shows the interactive effect of concentration and pH for BDHAC. The response contour plots of mutual interactions among the variables were found to be elliptical. Similar types of trends were found in literature [19] for dyes' removal. The optimum

Table 5
Optimum values of the variables for maximum % exhaustion

Parameter	Optimum values	
	CPC	BDHAC
pH	10.83	10.95
Temperature (°C)	79	85
Concentration (%omf)	1.63	1.85
Time (min)	57	77

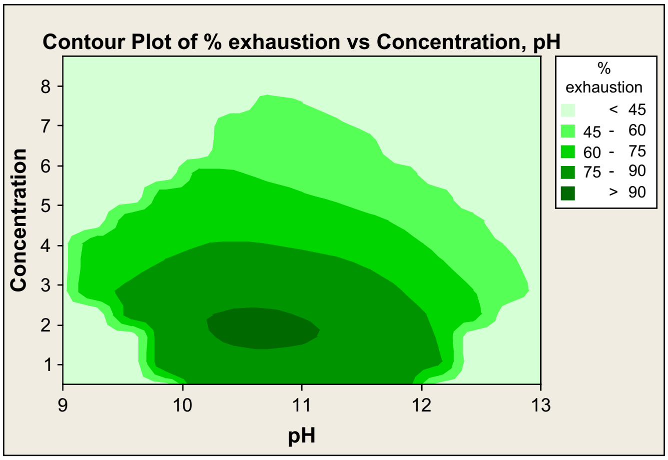

Fig. 6. Response contour plot of CPC % exhaustion onto nylon 66 showing interactive effects of pH and concentration.

values drawn from these figures are in close agreement with those obtained by optimizing the regression model Eqs. (5) and (6) using Monte-Carlo techniques. This confirms that the RSM could be effectively used to optimize the process variables using the statistical design of experiments concept. Experiments were carried out at the optimum conditions obtained by the theoretical analysis and highly feasible results were obtained that are tabulated in Table 5.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using Analysis of Variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [19]. According to the ANOVA, which is shown in Tables 6 and 7 for CPC and BDHAC, respectively, the $F_{statistics}$ values for all regressions were higher.

The large value of $F_{statistics}$ indicates that most of the variation in the response can be explained by the regression model equation. The associated P-value is used to estimate whether $F_{statistics}$ is large enough to indicate statistical significance. A P-value less than 0.0001 (i.e., $\alpha = 0.0001$, or 99.99% confidence interval) indicates that the model is considered to be statistically significant [19].

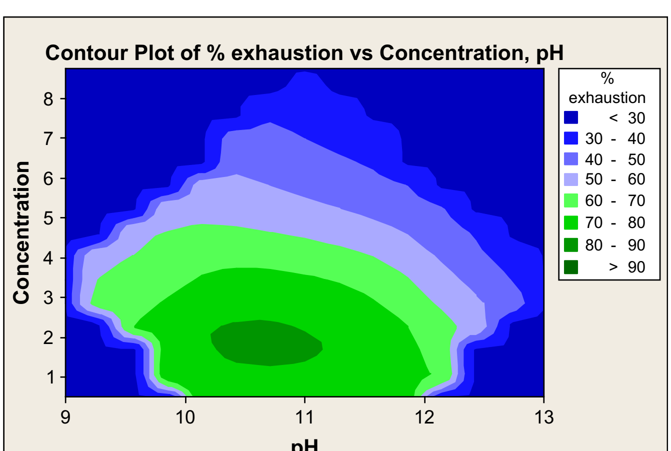

Fig. 7. Response contour plot of BDHAC % exhaustion onto nylon 66 showing interactive effects of pH and concentration.

Table 6
ANOVA for % exhaustion of CPC onto nylon polymer

Source	Degrees of freedom (df)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	14	9676.15	154	654.25	0.000
Linear	4	6832.27	1483.67	351.11	0.000
Square	4	6832.27	600.225	568.18	0.000
Interaction	6	442.98	73.830	69.89	0.000
Residual error	16	16.90	1.056		
Lack of fit	10	16.90	1.690		
Pure error	6	0.00	0.00		
Total	30	9693.06			

The P-values for all of the regressions were lower than 0.0001. This means that almost all the terms in the regression equation have a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct. The $F_{statistics}$ values of 251.02 for CPC and 654.25 for BDHAC are greater than tabulated $F_{14,16}$ values which indicate that the fitted model exhibits no lack of fit (0.0000001 for both CPC and BDHAC) at the confidence level. ANOVA for CPC and BDHAC, respectively, indicated that the second-order polynomial model (Eqs. (5) and (6)) was highly significant and adequate to represent the actual relationship between the response (% exhaustion) and the variables, with zero P-value for CPC as well as BDHAC and a very high coefficient of determination ($R^2 = 0.9996$ for CPC and $R^2 = 0.9989$ for BDHAC). This implies that 99.96% and 99.89% of the sample variation for CPC and BDHAC are explained by the independent variables and this also means that the model did not explain only about 0.04% and 0.11% of sample variation for CPC and BDHAC, respectively.

4. Conclusions

The ionic interactions between QAS and nylon polymer by reacting with carboxylic end groups under alkaline conditions were successfully carried out. The interactions between QAS

Table 7
ANOVA for % exhaustion of BDHAC onto nylon polymer

Source	Degrees of freedom (df)	Sum of squares (SS)	Mean square (MS)	$F_{statistics}$	P
Regression	14	9825.67	701.834	251.02	0.000
Linear	4	7143.39	367.754	131.53	0.000
Square	4	2207.25	551.812	197.37	0.000
Interaction	6	475.03	79.17	28.32	0.000
Residual error	16	44.73	2.796		
Lack of fit	10	44.73	4.473		
Pure error	6	0.00	0.00		
Total	30	9870.41			

and nylon polymer could provide improved antimicrobial functions of the nylon. A new methodology i.e., statistical experimental design was applied to study the linear, quadratic and interaction effects of the each of the variables and also to optimize those variables. A 2^4 response surface central composite design was successfully employed for experimental design and analysis of results. Appropriate empirical model equations were developed for predicting the % exhaustion for both CPC and BDHAC using response surface methodology. Graphical response contour plots were used to locate the optimum points.

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