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On the production optimization of polyacrylonitrile electrospun nanofiber

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Response surface methodology (RSM) based on central composite design (CCD) was employed to model and optimize the electrospinning parameters such as solution concentration (wt.%), applied voltage (kV), tip to collector distance (cm), and volume flow rate (ml/h), that have important effects on average fiber diameter (AFD) and contact angle (CA) of nanofiber mat. It is observed that polymer solution played an important role to the AFD and CA of nanofibers. Analysis of variance (ANOVA) showed a high determination coefficient (R^2) value of 0.9640 and 0.9683 for AFD and CA respectively, which indicated that the both models have a good agreement with experimental data. According to model optimization of the process, the minimum CA of electrospun fiber mat is given by following conditions: 13.2 wt.% solution concentration, 16.5 kV of the applied voltage, 10.6 cm of tip to collector distance, and 2.5 ml/h of volume flow rate.

Keywords: Electrospinning, Average fiber diameter, Contact angle, Response surface methodology

1. INTRODUCTION

Recently, it was demonstrated that electrospinning can produce superfine fiber ranging from micrometer to nanometer using an electric field force. In the electrospinning process, a strong electric field is applied between polymer solution contained in a syringe with a capillary tip and grounded collector. When the electric field overcomes the surface tension force, the charged polymer solution forms a liquid jet and travels towards collection plate. As the jet travels through the air, the solvent evaporates and dry fibers deposits on the surface of a collector [1-4].

The electrospun nanofibers have high specific surface area, high porosity, and small pore size. Therefore, they have been suggested as excellent candidate for many applications including filtration, multifunctional membranes, tissue engineering, protective clothing, reinforced composites, and hydrogen storage [5,6].

Studies have shown that the morphology and the properties of the electrospun nanofibers depend on many parameters including polymer solution properties (the concentration, liquid viscosity, surface tension, and dielectric properties of the polymer solution), processing parameters (applied voltage, volume flow rate, tip to collector distance, and the strength of the applied electric field), and ambient conditions (temperature, atmospheric pressure and humidity) [5-8].

Response surface methodology (RSM) is a combination of mathematical and statistical techniques used to evaluate the relationship between a set of controllable experimental factors and observed results. This optimization process is used in situations where several input variables influence some output variables of the system. The main goal of RSM is to optimize the response, which is influenced by several independent variables, with minimum number of experiments [9,10]. Therefore, the application of RSM in electrospinning process will be helpful in effort to find and optimize the electrospun nanofibers properties.

In this paper, a study has been conducted to investigate the relationship between four electrospinning parameters (solution concentration, applied voltage, tip to collector distance, and volume flow rate) and electrospun PAN nanofiber mat properties such as average fiber diameter (AFD) and contact angle (CA). and combined effects of above parameters. Then, these independent parameters were fed as inputs to an ANN while the output of the network was the CA of electrospun fiber mat. Finally, the importance of each electrospinning parameters on the variation of CA of electrospun fiber mat was determined and comparison of predicted CA value using RSM and ANN are discussed.

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2. EXPERIMENTAL

2.1. Materials

Polyacrylonirile (PAN, M_w=100,000) was purchased from Polyacryle Co. (Iran) and *N-N*, dimethylformamide (DMF) was obtained from Merck Co. (Germany).

The polymer solutions with different concentration ranged from 10 wt.% to 14 wt.% were prepared by dissolving PAN powder in DMF and was stirred for 24 h at 50°C. These polymer solutions were used for electrospinning.

2.2. Electrospinning

A schematic of the electrospinning apparatus is shown in Figure 1. A polymer solution was loaded in a 5 mL syringe connected to a syringe pump. The tip of the syringe was connected to a high voltage power supply (capable to produce 0-40 kV). Under high voltage, a fluid jet was ejected from the tip of the needle and accelerated toward the grounded collector (aluminum foil). All electrospinnings were carried out at room temperature.

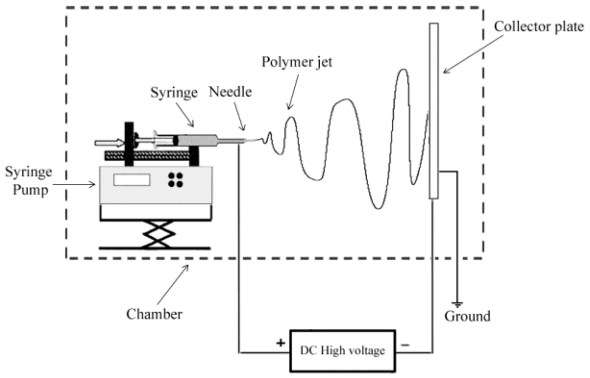

Fig. 1. Schematic of electrospinning set up.

2.3. Measurement and characterization

The electrospun nanofibers were sputter-coated with gold and their morphology was examined with a scanning electron microscope (SEM, Philips XL-30). Average diameter of electrospun nanofibers was determined from selected SEM image by measuring at least 50 random fibers using Image J software.

The wettability of electrospun fiber mat was determined by water contact angle measurement. Contact angles were measured by specially arranged microscope equipped with camera and PCTV vision software as shown in Figure 2. The volume of the distilled water for each measurement was kept at 1 µl.

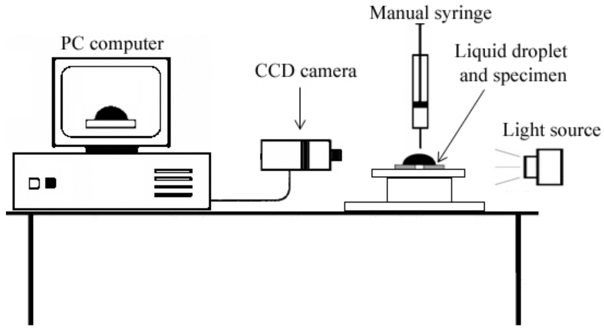

Fig. 2. Schematic of contact angle measurement set up.

2.4. Experimental design by RSM

In this study, the effect of four electrospinning parameters on two responses, comprising the AFD and the CA of electrospun fiber mat, was evaluated using central composite design (CCD). The experiment was performed for at least three levels of each factor to fit a quadratic model. Polymer solution concentration (X_1), applied voltage (X_2), tip to collector distance (X_3), and volume flow rate (X_4) were chosen as independent variables and the AFD and the CA of electrospun fiber mat as dependent variables (responses). The experimental parameters and their levels are given in Table 1.

Table 1. Design of experiment (factors and levels).

Factor	Variable	Unit	Factor level		
			-1	0	1
X_1	Solution concentration	(wt.%)	10	12	14
X_2	Applied voltage	(kV)	14	18	22
X_3	Tip to collector distance	(cm)	10	15	20
X_4	Volume flow rate	(ml/h)	2	2.5	3

A quadratic model, which also includes the linear model, is given below:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=2}^{4} \beta_{ij} x_i x_j \quad (1)$$

where, Y is the predicted response, x_i and x_j are the independent variables, β_0 is a constant, β_i is the linear coefficients, β_{ii} is the squared coefficients and β_{ij} is the second-order interaction coefficients [9,10].

The statistical analysis of experimental data was performed using Design-Expert software (Version 8.0.3, Stat-Ease, Minneapolis, MN, 2010) including analysis of variance (ANOVA). A design of 30 experiments for independent variables and responses for AFD and CA are listed in Table 2.

Table 2. The actual design of experiments and responses for AFD and CA.

No.	Electrospinning parameters				Responses	
	X_1 Concentration	X_2 Voltage	X_3 Distance	X_4 Flow rate	AFD (nm)	CA (°)
1	10	14	10	2	206±33	44±6
2	10	22	10	2	187±50	54±7
3	10	14	20	2	162±25	61±6
4	10	22	20	2	164±51	65±4
5	10	14	10	3	225±41	38±5
6	10	22	10	3	196±53	49±4
7	10	14	20	3	181±43	51±5
8	10	22	20	3	170±50	56±5
9	10	18	15	2.5	188±49	48±3
10	12	14	15	2.5	210±31	30±3
11	12	22	15	2.5	184±47	35±5
12	12	18	10	2.5	214±38	22±3
13	12	18	20	2.5	205±31	30±4
14	12	18	15	2	195±47	33±4
15	12	18	15	3	221±23	25±3
16	12	18	15	2.5	199±50	26±4
17	12	18	15	2.5	205±31	29±3
18	12	18	15	2.5	225±38	28±5
19	12	18	15	2.5	221±23	25±4
20	12	18	15	2.5	215±35	24±3
21	12	18	15	2.5	218±30	21±3
22	14	14	10	2	255±38	31±4
23	14	22	10	2	213±37	35±5
24	14	14	20	2	240±33	33±6
25	14	22	20	2	200±30	37±4
26	14	14	10	3	303±36	19±3
27	14	22	10	3	256±40	28±3
28	14	14	20	3	283±48	39±5
29	14	22	20	3	220±41	36±4
30	14	18	15	2.5	270±43	20±3

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3. RESULTS AND DISCUSSION

3.1. Morphological analysis of nanofibers

PAN solution in DMF were electrospun under different conditions, including various PAN solution concentrations, applied voltages, volume flow rates and tip to collector distances, to study the effect of electrospinning parameters on the morphology and properties of electrospun nanofibers.

Figure 3 shows the SEM images and fiber diameter distributions of electrospun fibers in different solution concentration as one of the most effective parameters to control the fiber morphology. As observed in Figure 3, the AFD increased with increasing solution concentration. It was suggested that the higher solution concentration would have more polymer chain entanglements and less chain mobility. This causes the hard jet extension and disruption during electrospinning process and producing thicker fibers.

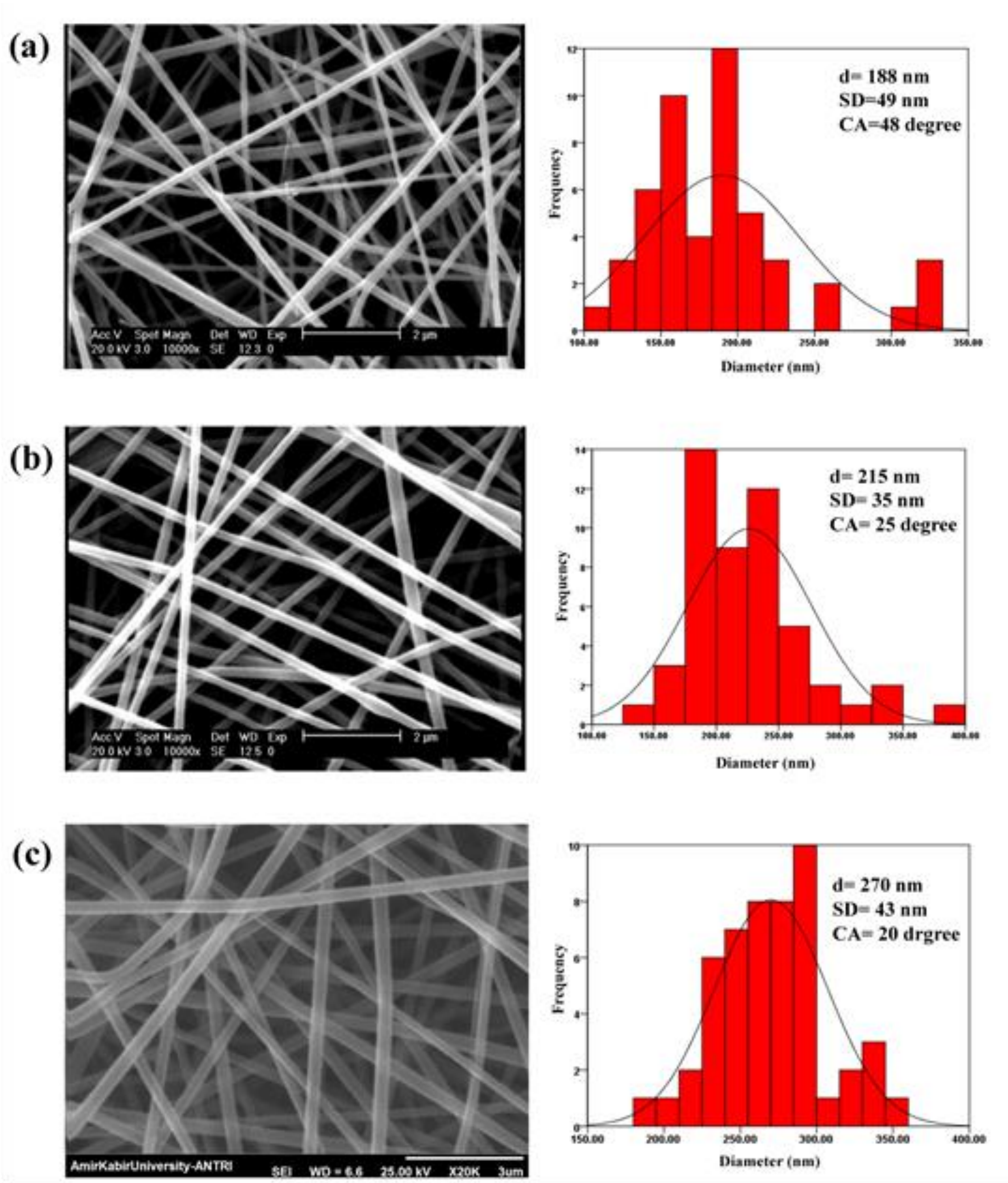

Fig. 3. The SEM images and fiber diameter distributions of electrospun fibers in solution concentration of (a) 10 wt.%, (b) 12 wt.% and (c) 14 wt.%.

The SEM image and corresponding fiber diameter distribution of electrospun nanofiber in different applied voltage are shown in Figure 4. It is obvious that increasing the applied voltage cause an increase followed by a decrease in electrospun fiber diameter. As demonstrated by previous researchers [7,8], increasing the applied voltage may decrease, increase or may not change the fiber diameter. In one hand, increasing the applied voltage will increase the electric field strength and higher electrostatic repulsive force on the jet, favoring the thinner fiber formation. On the other hand, more surface charge will introduce on the jet and the solution will be removed more quickly from the tip of needle. As a result, the AFD will be increased [8,11].

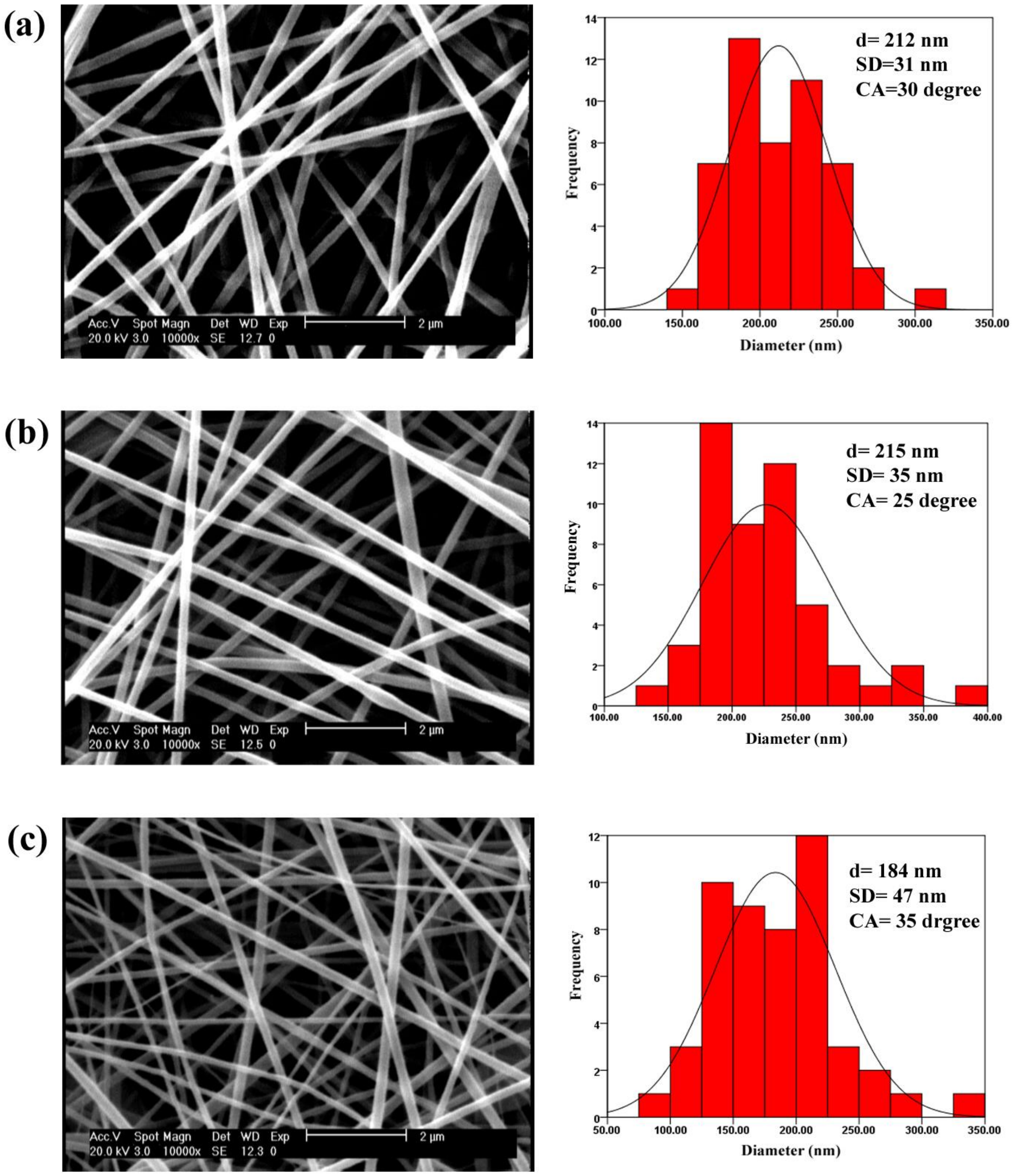

Fig. 4. The SEM images and fiber diameter distributions of electrospun fibers in applied voltage of (a) 14 kV, (b) 18 kV and (c) 22 kV.

Figure 5 represents the SEM image and fiber diameter distribution of electrospun nanofiber in different spinning distance. It can be seen that the AFD decreased with increasing tip to collector distance. Because of the longer spinning distance could give more time for the solvent to evaporate, increasing the spinning distance will decrease fiber diameter [3,8].

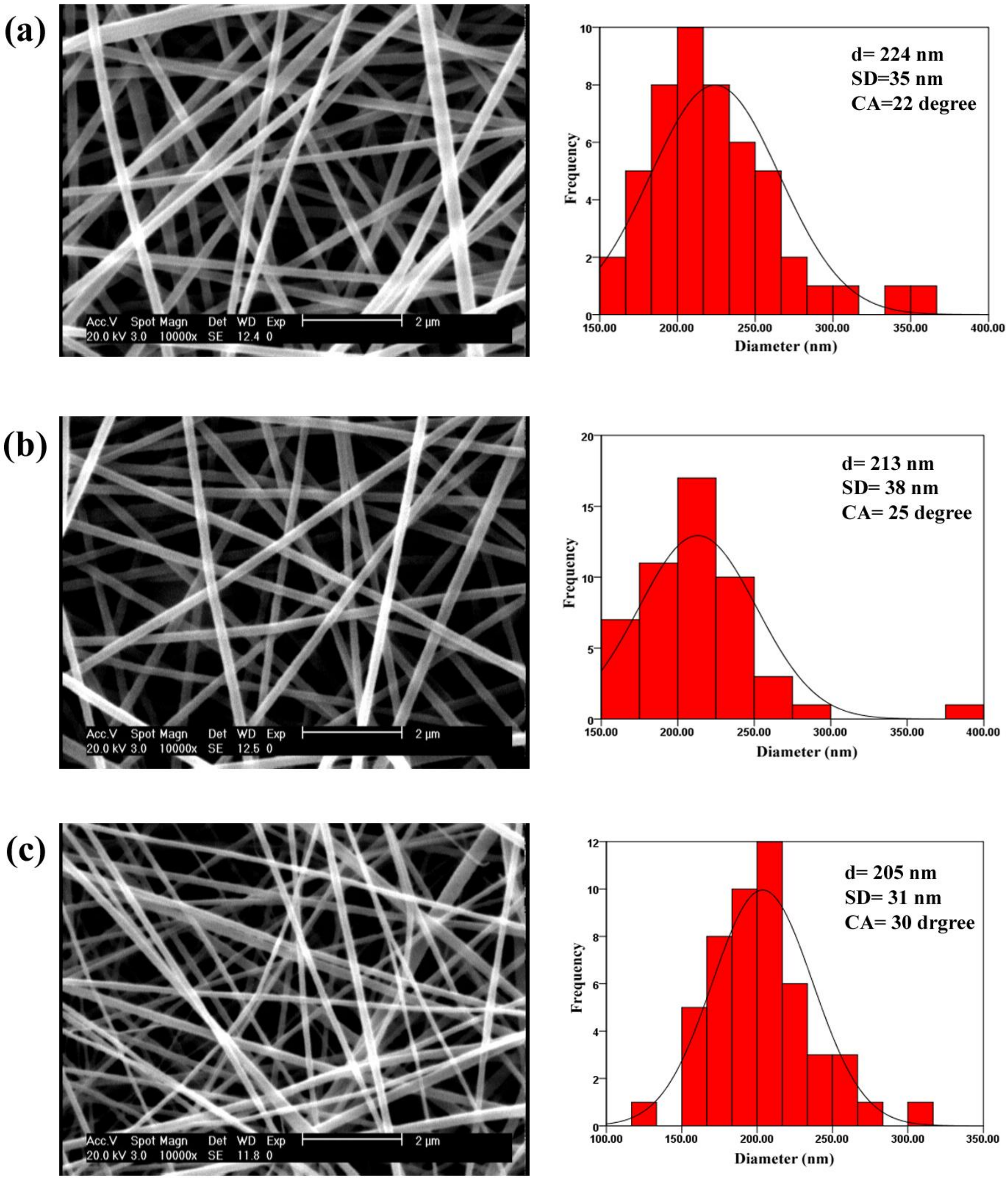

Fig. 5. The SEM images and fiber diameter distributions of electrospun fibers in tip to collector distance of (a) 10 cm, (b) 15 cm and (c) 20 cm.

The SEM image and fiber diameter distribution of electrospun nanofiber in different volume flow rate are illustrated in Figure 6. It is clear that increasing the volume flow rate cause an increase in average fiber diameter. Ideally, the volume flow rate must be compatible with the amount of solution removed from the tip of the needle. At low volume flow rates, solvent would have sufficient time to evaporate and thinner fibers were produced, but at high volume flow rate, excess amount of solution fed to the tip of needle and thicker fibers result [3,12].

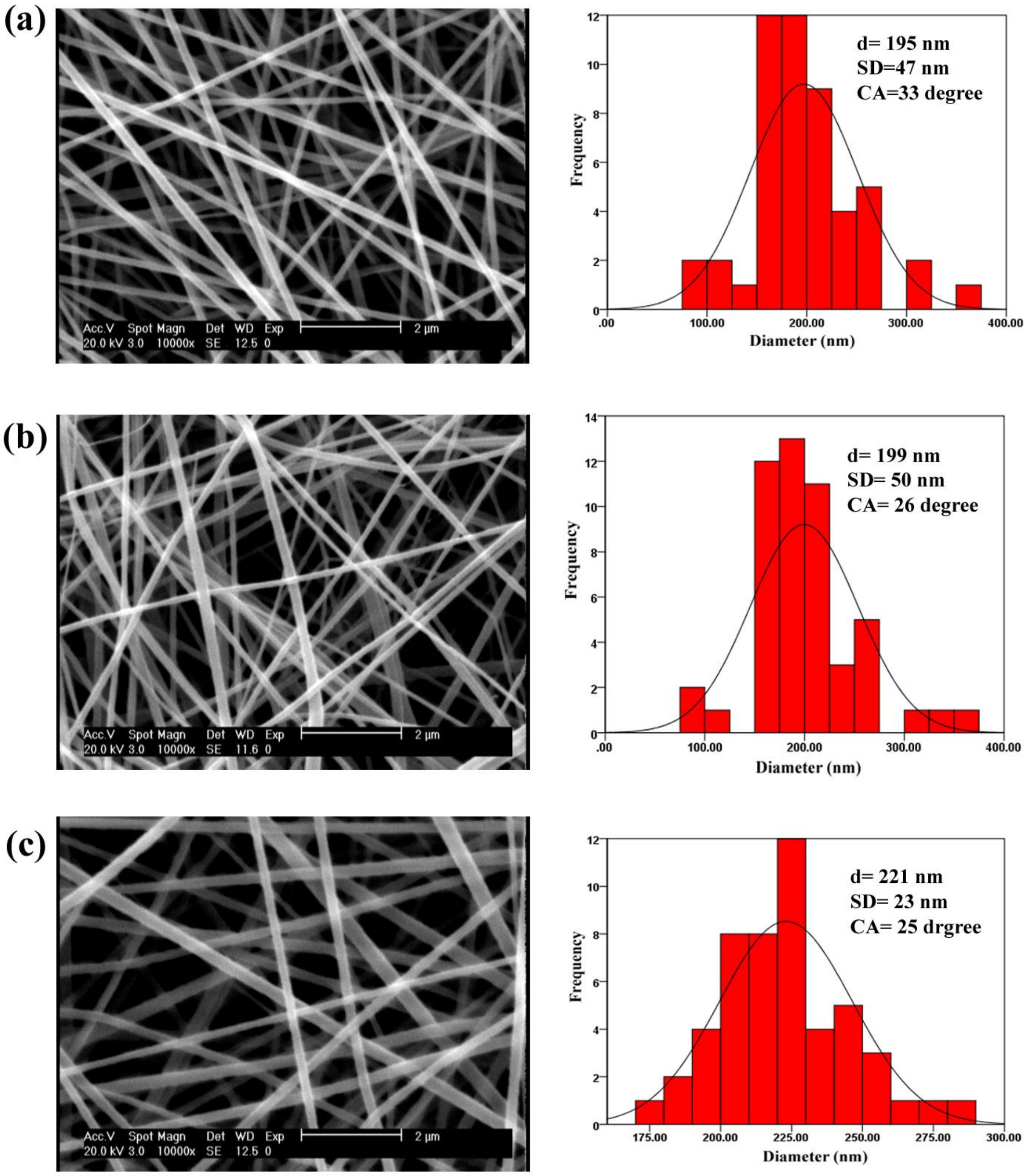

Fig. 6. The SEM images and fiber diameter distributions of electrospun fibers in volume flow rate of (a) 2 ml/h, (b) 2.5 ml/h and (c) 3 ml/h.

3.2. The analysis of variance (ANOVA)

The analysis of variance for AFD and CA of electrospun fibers has been summarized in Table 3 and Table 4 respectively, which indicated that the predictability of the models is at 95% confidence interval. Using 5% significance level, the factor is considered significant if the p-value is less than 0.05.

From the p-values presented in Table 3 and Table 4, it is obvious that p-values of terms X_3^2, X_4^2, X_2X_3, X_1X_3, X_2X_4 and X_3X_4 in the model of AFD and X_3^2, X_4^2, X_2X_3, X_2X_4 and X_3X_4 in the model of CA were not significant (p>0.05).

The approximating function for AFD and CA of electrospun fiber obtained from Equation 2 and 3 respectively.

$$AFD = 211.89 + 31.71X_1 - 15.28X_2 - 12.78X_3 + 12.94X_4 - 8.44X_1X_2 + 6.31X_1X_4 + 18.15X_1^2 - 13.85X_2^2 \quad (2)$$

$$CA = 26.07 - 9.89X_1 - 2.17X_2 + 4.33X_3 2.33X_4 - 1.63X_1X_2 - 1.63X_1X_3 + 1.63X_1X_4 + 9.08X_1^2 + 7.58X_2^2 \quad (3)$$

Analysis of variance for AFD and CA showed that the models were significant (p<0.0001), which indicated that the both models have a good agreement with experimental data. The value of determination coefficient (R^2) for AFD and CA was evaluated as 0.9640 and 0.9683 respectively.

The predicted versus actual response plots of AFD and CA are shown in Figures 7 and 8 respectively. It can be observed that experimental values are in good agreement with the predicted values.

Table 3. Analysis of variance for average fiber diameter (AFD).

Source	SS	DF	MS	F-value	Probe > F	Remarks
Model	31004.72	14	2214.62	28.67	<0.0001	Significant
X_1-Concentration	17484.50	1	17484.50	226.34	<0.0001	Significant
X_2-Voltage	4201.39	1	4201.39	54.39	<0.0001	Significant
X_3-Distance	2938.89	1	2938.89	38.04	<0.0001	Significant
X_4-Flow rate	3016.06	1	3016.06	39.04	<0.0001	Significant
X_1X_2	1139.06	1	1139.06	14.75	0.0016	Significant
X_1X_3	175.56	1	175.56	2.27	0.1524	
X_1X_4	637.56	1	637.56	8.25	0.0116	Significant
X_2X_3	39.06	1	39.06	0.51	0.4879	
X_2X_4	162.56	1	162.56	2.10	0.1675	
X_3X_4	60.06	1	60.06	0.78	0.3918	
X_1^2	945.71	1	945.71	12.24	0.0032	Significant
X_2^2	430.80	1	430.80	5.58	0.0322	Significant
X_3^2	0.40	1	0.40	0.0052	0.9433	
X_4^2	9.30	1	9.30	0.12	0.7334	
Residual	1158.75	15	77.25			
Lack of Fit	711.41	10	71.14	0.80	0.6468	

Table 4. Analysis of variance for contact angle (CA) of electrospun fiber mat.

Source	SS	DF	MS	F-value	Probe > F	Remarks
Model	4175.07	14	298.22	32.70	<0.0001	Significant
X_1-Concentration	1760.22	1	1760.22	193.01	<0.0001	Significant
X_2-Voltage	84.50	1	84.50	9.27	0.0082	Significant
X_3-Distance	338.00	1	338.00	37.06	<0.0001	Significant
X_4-Flow rate	98.00	1	98.00	10.75	0.0051	Significant
X_1X_2	42.25	1	42.25	4.63	0.0481	Significant
X_1X_3	42.25	1	42.25	4.63	0.0481	Significant
X_1X_4	42.25	1	42.25	4.63	0.0481	Significant
X_2X_3	12.25	1	12.25	1.34	0.2646	
X_2X_4	6.25	1	6.25	0.69	0.4207	
X_3X_4	2.25	1	2.25	0.25	0.6266	
X_1^2	161.84	1	161.84	17.75	0.0008	Significant
X_2^2	106.24	1	106.24	11.65	0.0039	Significant
X_3^2	0.024	1	0.024	0.0026	0.9597	
X_4^2	21.84	1	21.84	2.40	0.1426	
Residual	136.80	15	9.12			
Lack of Fit	95.30	10	9.53	1.15	0.4668	

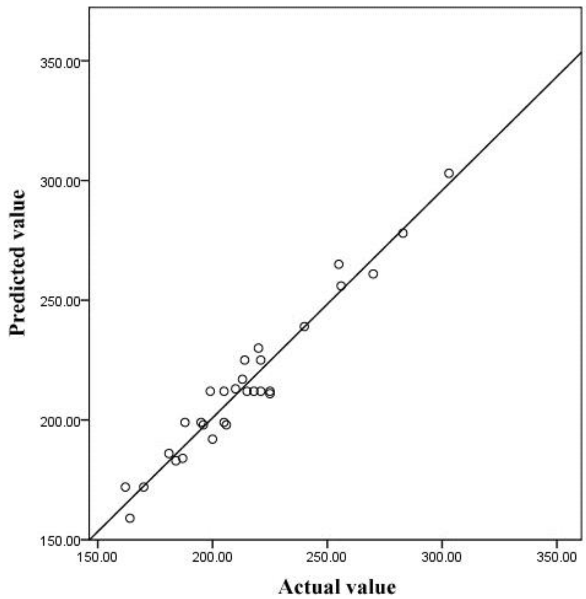

Fig. 7. The predicted versus actual plot for AFD of electrospun fiber mat.

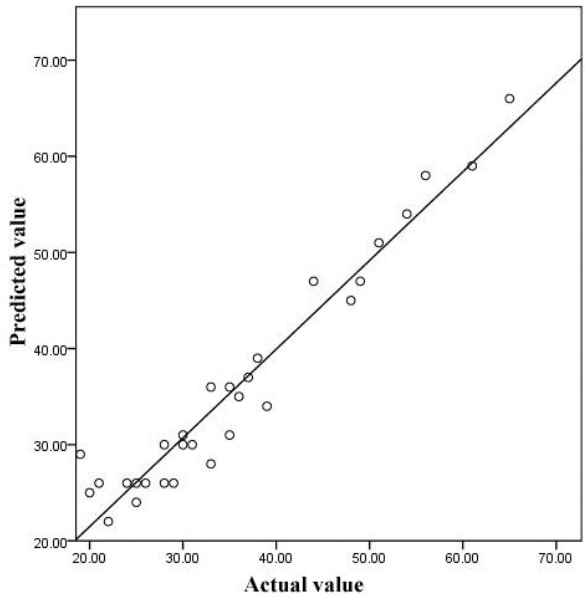

Fig. 8. The predicted versus actual plot for CA of electrospun fiber mat.

3.3. Effects of significant parameters on AFD

The response surface and contour plots in Figure 9 (a) indicated that there was a considerable interaction between solution concentration and applied voltage at middle level of spinning distance (15 cm) and flow rate (2.5 ml/h). It can be seen an increase in AFD with increase in solution concentration at any given voltage that is in agreement with previous observations [11,12]. Generally, a minimum solution concentration is required to obtain uniform fibers from electrospinning. Below this concentration, polymer chain entanglements are insufficient and a mixture of beads and fibers is obtained. On the other hand, the higher solution concentration would have more polymer chain entanglements and less chain mobility. This causes the hard jet extension and disruption during electrospinning process and producing thicker fibers [7].

Figure 9 (b) shows the response surface and contour plots of interaction between solution concentration and flow rate at fixed voltage (18 kV) and spinning distance (15 cm). It can be seen that at fixed applied voltage and spinning distance, an increase in solution concentration and volume flow rate results in fiber with higher diameter. As mentioned in the literature, the volume flow rate must be compatible with the amount of solution removed from the tip of the needle. At low volume flow rates, solvent would have sufficient time to evaporate and thinner fibers were produced, but at high volume flow rate, excess amount of solution fed to the tip of needle and thicker fibers were resulted [3,8].

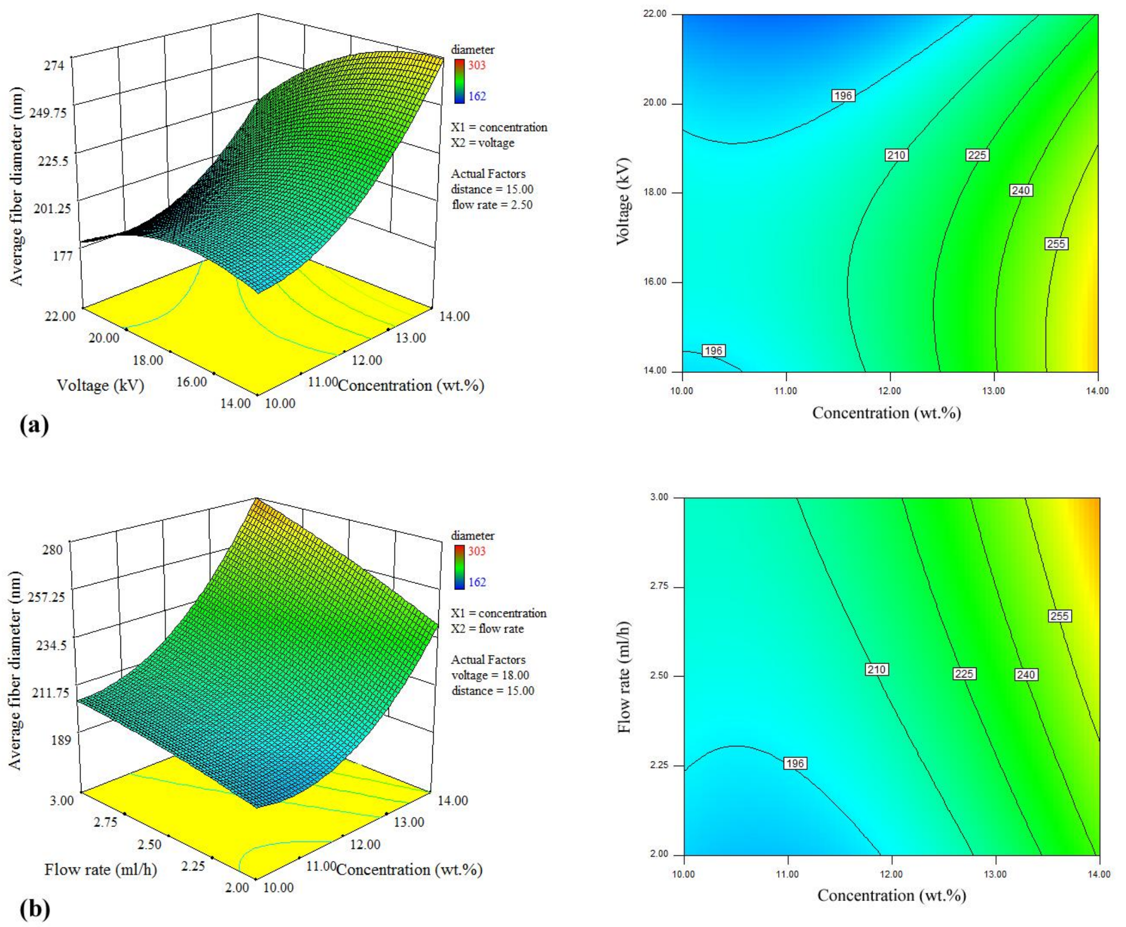

Fig. 9. Response surface and contour plots of AFD showing the effect of: (a) solution concentration and applied voltage, (b) solution concentration and volume flow rate.

3.4. Effects of significant parameters on CA

The response surface and contour plots in Figure 10 (a) represented the CA of electrospun fiber mat at different solution concentration and applied voltage. It is obvious that at fixed spinning distance and volume flow rate, an increase in applied voltage and decrease in solution concentration result the higher CA. The tip to collector distance was found to be another important processing parameter as it influences the solvent evaporating rate and deposition time as well as electrostatic field strength. The impact of spinning distance on CA of electrospun fiber mat is illustrated in Figure 10 (b). Increasing the spinning distance causes the CA of electrospun fiber mat to increase. As demonstrated in Figure 10 (b), low solution concentration cause an increase in CA of electrospun fiber mat at large spinning distance. The response plots in Figure 10 (c) shows the interaction between solution concentration and volume flow rate at fixed applied voltage and spinning distance. It is obvious that at any given flow rate, CA of electrospun fiber mat will increase as solution concentration decreases.

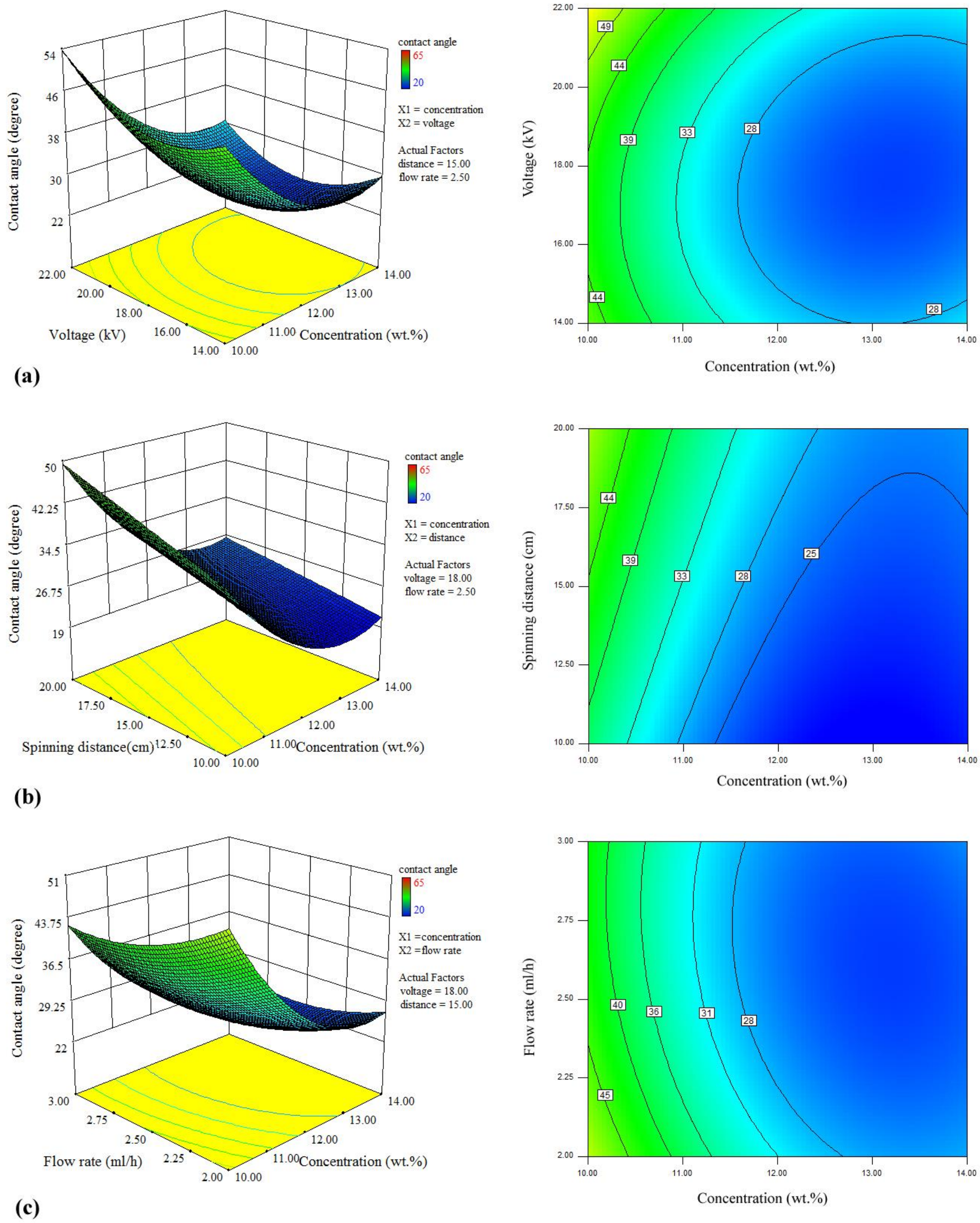

Fig. 10. Response surface and contour plots of CA showing the effect of: (a) solution concentration and applied voltage, (b) solution concentration and spinning distance, (c) solution concentration and volume flow rate.

3.5. Determination of optimal conditions

It is well known that the value of CA for hydrophilic surfaces is less than 90º. Fabrication of these surfaces has attracted considerable interest for both fundamental research and practical studies. So, the goal of the present study is to minimize the CA of electrospun nanofibers. The optimal conditions of the electrospinning parameters were established from the quadratic form of the RSM. Independent variables namely, solution concentration, applied voltage, spinning distance, and volume flow rate were set in range and dependent variable (CA) was fixed at minimum. The optimal conditions in the tested range for minimum CA of electrospun fiber mat are shown in Table 5.

Table 5. Optimum values of the process parameters for minimum CA of electrospun fiber mat.

Parameter	Optimum value
Solution concentration (wt.%)	13.2
Applied voltage (kV)	16.5
Spinning distance (cm)	10.6

This optimum condition was a predicted value, thus to confirm the predictive ability of the RSM model for response, a further electrospinning was carried out according to the optimized conditions and the agreement between predicted and measured responses was verified. The measured CA of electrospun nanofiber mat (21º) was very close to the predicted value estimated to 20º. Figure 11 shows the SEM image and AFD distribution of electrospun fiber mat prepared at optimized conditions.

4. CONCLUSIONS

In this study, the effects of electrospinning parameters, comprising solution concentration (wt.%), applied voltage (kV), tip to collector distance (cm), and volume flow rate (ml/h) on average diameter and CA of electrospun PAN nanofibers were investigated by statistical approach. Response surface methodology (RSM) was successfully employed to model and optimize the electrospun nanofibers diameter and CA. The response surface and contour plots of the predicted AFD and CA indicated that the nanofiber diameter and its CA are very sensitive to solution concentration changes. It was concluded that the polymer solution concentration was the most significant factor impacting the AFD and CA of electrospun fiber mat. The R^2 value was 0.9640 and 0.9683 for AFD and CA respectively, which indicates a good fit of the models with experimental data. The optimum value of the solution concentration, applied voltage, spinning distance, and flow rate were found to be 13.2 wt.%, 16.5 kV, 10.6 cm and 2.5 ml/h, respectively, for minimum CA of electrospun fiber mat.

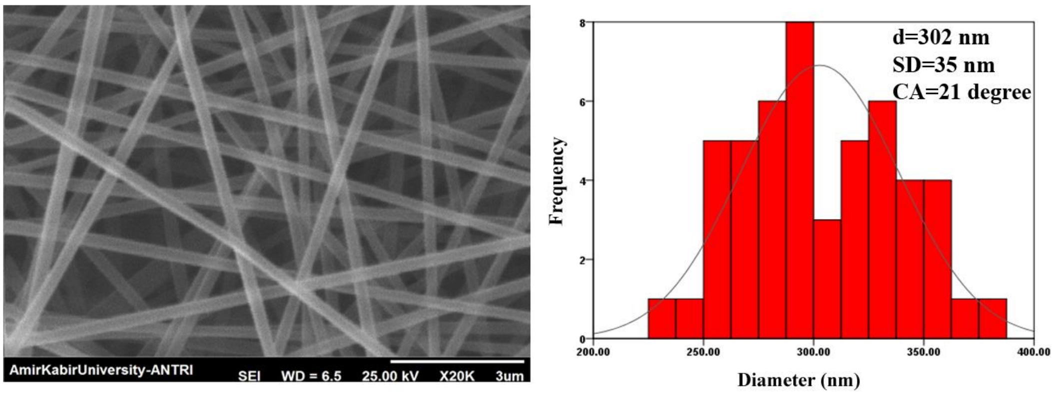

Fig. 11. SEM image and fiber diameter distribution of electrospun fiber mat prepared at optimized conditions.

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ОТНОСНО ОПТИМИЗАЦИЯТА НА ПРОИЗВОДСТВОТО НА ЕЛЕКТРОПРЕДЕНИ НАНОВЛАКНА ОТ ПОЛИАКРИЛАМИД

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(Резюме)

Приложена е методология на повърхнината на отклика (RSM), основана на централно композиционен планиран експеримент за моделирането и оптимизацията на параметрите на електропредене – концентрация на разтворите (тегл. %), приложеното напрежение (kV), разстоянието от дюзата до приемника (cм) и обемния дебит (ml/h), имащи важно значение за средния диаметър на влакната (AFD) и контактния ъгъл на с подложката (CA). Отбелязано е, че полимерните разтвори имат важна роля за AFD и за CA при нановлакната. Анализът на дисперсията показва висок коефициент на корелация от 0.9640 и съответно 0.9683 за AFD и CA, което показва че двата модела се съгласуват добре с опитните данни. Според моделирането на процеса минимален контактен ъгъл с подложката за електропредените влакна се наблюдава при следните условия: концентрация на разтвора - 13.2 тегл.%, приложено напрежение - 16.5 kV; разстояние от дюзата то приемника - , 10.6 cm и обемен дебит на потока - 2.5 ml/h.