Prediction of Water Retention Capacity of Hydrolysed Electrospun Polyacrylonitrile Fibers Using Statistical Model and Artificial Neural Network

Venkateshwarapuram Rengaswami Giri Dev,[1,2] Jayarama Reddy Venugopal,[1] Muthusamy Senthilkumar,[3] Deepika Gupta,[1] Seeram Ramakrishna[1]

[1]*Division of Bioengineering, Nanoscience and Nanotechnology Initiative, National University of Singapore, Singapore 117576*
[2]*Department of Textile Technology, A.C. College of Technology, Anna University, Chennai 625025*
[3]*Department of Textile Technology, P.S.G. College of Technology, Coimbatore 641004*

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ABSTRACT: Box Behnken design of experiment was used to study the effect of process variables such as alkali concentration, temperature and time on water retention capacity of the alkaline hydrolysed electrospun fibres. The hydrolysis of electrospun polyacrylonitrile fibres was carried out using sodium hydroxide with different processing conditions like concentration of alkali, temperature and time. With the increase in the concentration of alkali, time and temperature, the water retention capacity of membrane was found to increase in the membranes. Water retention capacities of the membranes were modeled and predicted using empirical as well as artificial neural network (ANN model). The fiber diameter and mean flow pore diameter of electrospun polyacrylonitrile fibers and hydrolyzed fibers shown in SEM images were 310 ± 50, 275 ± 75 nm, 0.9258 and 1.12 microns, respectively. The present study indicated that the nanofibrous membranes have potential for the water absorbing applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3397–3404, 2009

Key words: electrospinning; nanofibers; hydrolysis; neural network; statistical model

INTRODUCTION

Around the globe, approximately 2.73 million tons of polyacrylonitrile fibres (PAN) are produced per year[1] and they find interesting applications in clothing and industrial sectors. Acrylic fibres have been used in industrial applications such as precursors for the production of carbon fibres, water absorbents, ion exchange materials, and as antistatic fibers.[2] One of the reasons for versatility of these fibers in wide range of applications is due to the presence of high surface area to volume ratio of these fibres. Even though conventional fibre forming process such as melt spinning and solution spinning produces fibres, electrospinning technology has come out as boon in the hand of the researchers to produce fibres in the range of micrometer to nanometer. Electrospinning involves the application of high voltage to a droplet of polymeric solution resulting in the collection of nanofibrous web on the grounded collector. The nonwoven webs produced by this process possess high surface area to volume ratio, high porosity, and interconnectivity with controllable nonwoven thickness. They find interesting applications in the field of health, energy, environment, and defense applications such as super capacitors, biosensors, scaffolds for tissue engineering, wound dressing, fuel cells, water filters, face masks, and used as affinity membranes.[3–9]

Polyacrylonitrile fibers has been widely used to produce the nanofibers as they find applications in the production of carbon fibers, metal ion and organic solvents adsorption, photocatalytic degradation, antimicrobial filters, and as membranes.[10–15] One of the important applications of conventionally produced acrylic fibers is in the field of super absorbents and it has been reported that most of the super absorbent polymers exist in the form of sodium salt of polyacrylic acid, available as powder or in granular form and used mainly in personal care products such as baby diapers.[3] Hence considerable amount of research efforts are involved to produce water absorbent polymers by surface modification of acrylic fibers. Alkaline hydrolysis of acrylic fibers have been studied by various researchers but limited work has been carried out on alkaline hydrolysis of electrospun nanofibrous membranes.[16–18]

In the present work, a systematic statistical approach has been adopted to obtain optimum

Correspondence to: V. R. Giri Dev (vrgiridev@yahoo.com).
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TABLE I
The Box Behnken Experimental Design for the Three Independent Variables

Trial no.	Coded values of the variables		
	Alkali concentration (X_1)	Temperature (X_2)	Time (X_3)
1	0	1	−1
2	0	0	0
3	−1	0	1
4	−1	−1	0
5	−1	1	0
6	1	0	1
7	1	−1	0
8	0	−1	−1
9	0	−1	1
10	0	0	0
11	−1	0	−1
12	1	0	−1
13	1	1	0
14	0	1	1
15	0	0	0

water retention capacity of the electrospun membranes with different process conditions. The influence of process conditions on the water retention capacity of the electrospun membranes was carried out using Box Behnken experimental design. The design of experiment is an alternative and more efficient approach, which are increasingly being used in polymeric studies. The response surface methodology was used to develop a mathematical correlation between the alkali concentration, temperature and time on water retention capacity. Regression equations were developed for the same and in addition to that the effect of process conditions was also modeled using artificial neural network. Comparison of prediction of water retention capacity using ANN and statistical approach are discussed in this article.

EXPERIMENTAL

Materials

A commercially available acrylic fibre in the form of yarn (Nm 10) was used as such without any modification for the present study. Dimethyl Formamide (DMF) procured from Sigma Aldrich, USA was used as a solvent for the production of electrospun nanofibers.

Methods

Design of experiments

Experiments were conducted based on the Box Behnken second order design for three variables. In this experimental design Alkali Concentration (X_1), Temperature (X_2), and Time (X_3) were taken as independent variables. The variables were selected at three levels, which are −1, 0, +1. The response (Y) is given by a second order polynomial as shown below,

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i \geq j}^{k} \sum_{i=1}^{k} b_{ij} x_i x_j. \quad (1)$$

where Y = predicted response, b_0 = offset term, b_i = linear effect, b_{ii} = squared effect, b_{ij} = interaction effect.

The actual design experiment and the corresponding actual values for each variable are listed in Tables I and II, respectively.

The degree of experiments chosen for this study is Box Behnken experimental design of three independent variables. The design is applicable to the critical variables that have been identified and it is preferred because relatively few experimental combinations of the variables are needed to estimate potentially complex response functions. Fifteen experiments are needed to estimate the 10 sets of coefficients using multiple linear regression analysis. The above equation was solved using the design expert (State-Ease Statistics Made-Easy, Minneapolis, MN, Version 7.1.5, 2008) to estimate the response of the independent variables. All experiments were performed in duplicate. To obtain the optimum values of the independent variables, the regression equation was optimized following an iterative method.[19–23]

Preparation of electrospun membranes

The nonwoven electrospun nanofibrous membranes were prepared using a typical electrospinning setup with a syringe and flat plate collector assembly.[5] Commercially bought acrylic fibres was dissolved in dimethyl formamide (13% w/v) at 50°C. A constant voltage of 15 kV was applied to solution in the syringe needle and the solution was electrospun at the rate of 1 mL/h to a circular aluminium collector plate. The distance between the tip of the spinneret and the collector was fixed at 12 cm. The fibres were collected for 2 h at a constant humidity. The membranes were then separated from the aluminium foil and vacuumed for 10 days to remove the residual solvent present in the membrane. The morphology

TABLE II
Actual Values of the Variables for the Coded Values

Coded values	Uncoded values of the variables		
	Alkali concentration (w/v%) (X_1)	Temperature (°C) (X_2)	Time (min) (X_3)
−1	3	50	30
0	6	60	45
+1	9	70	60

of the electrospun nanofibers was observed using scanning electron microscope (SEM) at an accelerating voltage of 10 kV and the fiber diameter was measured with the SEM images using Image J software (National Institute of Health, USA).[5,6]

Alkaline hydrolysis of electrospun fibres

The electrospun nanofibrous membranes of uniform weight were cut into circular discs of diameter 2 cm and were placed in a glass tube containing the required amount of sodium hydroxide solution as per the experimental conditions given in Table I. After hydrolysis, the samples were washed with de-ionized water and dried under vacuum.

Water retention capacity

The electrospun samples were placed in de-ionized water for a period of 60 min. The samples were removed and centrifuged for 15 min at 1500 rpm, and then weighed. Water retention capacity was determined as the increase in the weight of the fibers. The experiments were carried out as per the procedure cited in the literature.[2]

Fourier transform infrared (FTIR) spectroscopy studies

The infrared spectra of the samples were recorded on a NICOLET POTRAGE 460 (LDA). Infrared studies were carried out in the range of 400–4000 cm^{-1}. The sample was dried in desiccators for 3 days before taking spectra. Spectra were taken immediately after the samples were taken outside the desiccator.

RESULTS AND DISCUSSION

Response surface methodology is an empirical modeling technique, which is used to evaluate the relationship between a set of controllable experimental factors and observed results. Several factors influence hydrolysis of electrospun acrylic nanofiber of which, alkali concentration, temperature and time play a vital role. To study the effect of these variables Box Behnken design is used. Treatments are carried out based on the experimental design given in Table I. The limits for the design in terms of concentration, temperature and time was fixed after careful consideration as suggested in literature at elevated temperature, time and temperature playing a significant degradation of membrane occurred leading to disintegration of the membrane.[18] Various empirical models were fitted to the response and lack of fit tests was carried out and the regression equation is given below taking into account the significant interaction effects as given in Table III.

TABLE III
Analysis of Variance for the Response Surface

Source	F	P (Prob > F)
X_1-concentration	414.6	0.0001
X_2-temperature	20.8	0.001
X_3-time	0.2	0.638
X_1X_2	4.3	0.071
X_1X_3	6.4	0.035
X_2X_3	1.9	0.204

$$\%\text{Water retention capacity} = +167.47 + 31.25X_1 + 7.00X_2 - 4.50X_1X_2 - 5.50X_1X_3.$$

The model F-value was 74.72 which implied that the model was significant and there was only 0.01% chance that a "Model F-Value" of this large value could occur due to noise. The Predicted R^2 value was 0.9130 and is in reasonable agreement with the Adjusted R^2 of 0.9693. Adequate precision which measures the signal to noise ratio was 27.063, which is greater than 4 indicating that the model can be used to navigate the design space.

"Artificial neural network" (ANN) is an information processing system that roughly replicates the behavior of a human brain by emulating the operations and connectivity of biological neurons. From a mathematical point of view, ANN is a complex nonlinear function with many parameters that are adjusted (calibrated or trained) in such a way that the ANN output becomes similar to that of measured output on a known data set. ANNs are typically composed of interconnected units which serve as model neurons. The function of the synapse is modeled by a modifiable weight, which is associated with each connection. Each unit converts the pattern of incoming activities in such a way that it reacts with a single outgoing activity and then broadcast it to other units. It performs this conversion in two stages. First, it multiplies each incoming activity called "total input." Second, an input output function and transforms the total input and outgoing activity. The commonest type of ANN consists of three groups or a layer of hidden units, which is connected to a layer of output units. The activity of the input units represents the raw information that is fed into the network. The activity of each hidden unit is determined by the activities of the input units and the weights on the connections between the input and hidden units. Similarly, the behavior of the output units depends on the activity of the hidden units and the weights between the hidden and output units.[24–26] The schematic diagram of typical

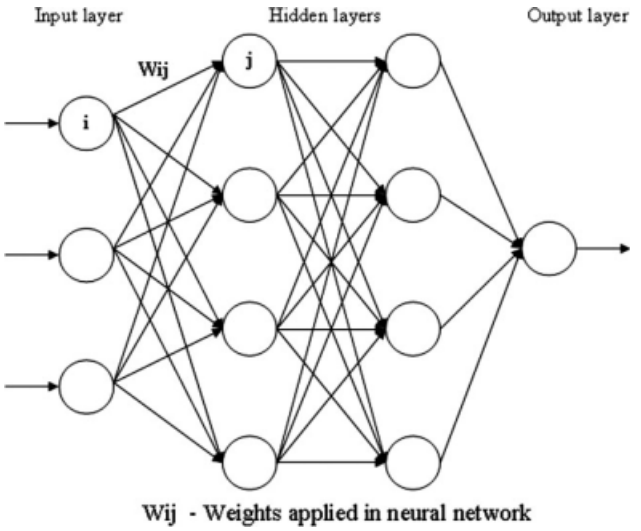

Figure 1 Artificial Neural Network.

ANN is shown in Figure 1. The experimental and predicted values using empirical and ANN model are given in Table IV and the comparison of results obtained from the empirical and ANN model are discussed in later section.

TABLE IV
Experimental and Predicted Values of Water Retention Capacity by Empirical and ANN Models

Trial no	Experimental	Predicted		Absolute error (%)	
		Empirical	ANN	Empirical	ANN
1	178	178	178	0.00	0.00
2	168	167	169	0.60	0.60
3	140	141	138	2.14	1.43
4	125	124	126	2.40	0.80
5	148	148	145	2.03	2.03
6	198	192	196	2.02	1.01
7	190	196	188	2.11	1.05
8	158	158	159	0.00	0.63
9	162	162	160	0.00	1.23
10	170	171	170	0.59	0.00
11	130	132	132	2.31	1.54
12	210	204	198	1.43	5.71
13	195	201	204	1.54	4.62
14	170	167	178	0.59	4.71
15	170	171	170	0.59	0.00
R^2 values		0.98	0.96		
Mean absolute percentage error				1.25	1.69
SD of absolute percentage error				1.23	1.82

Effect of temperature and time

Figure 2 shows the water retention capacity of the hydrolysed electrospun nanofibers at different temperature and time for constant alkali concentration (at minimum and maximum levels). From the figure, it can be seen that at any given time the water retention capacity increases with increasing the temperature and it can also be observed from the same figure that at a given reaction temperature, with increasing time the water retention capacity is increasing for lower concentration of alkali and while it is not the case at higher concentration. At higher concentration with longer duration of reaction, the water retention capacity decreased and it can be attributed to the significant weight loss (15%) occurred in the electrospun membrane as result of hydrolysis. Moreover, it should be mentioned that at higher concentration, the increase in temperature and time aids in faster hydrolysis resulting quick conversion of polymer chains into water soluble products. Similar kind of results has also been

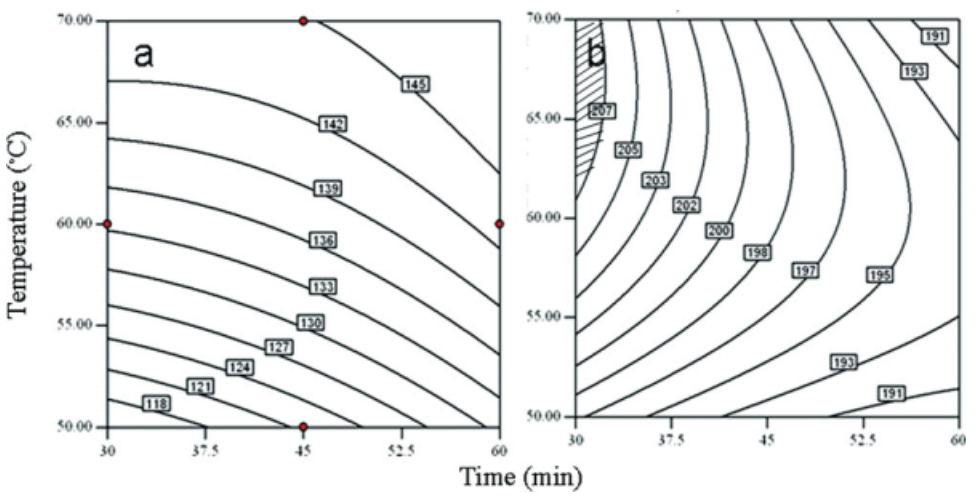

Figure 2 Effect of temperature and time on the water retention capacity (%) at various levels of concentration of alkali (a) 3% w/v and (b) 9% w/v. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

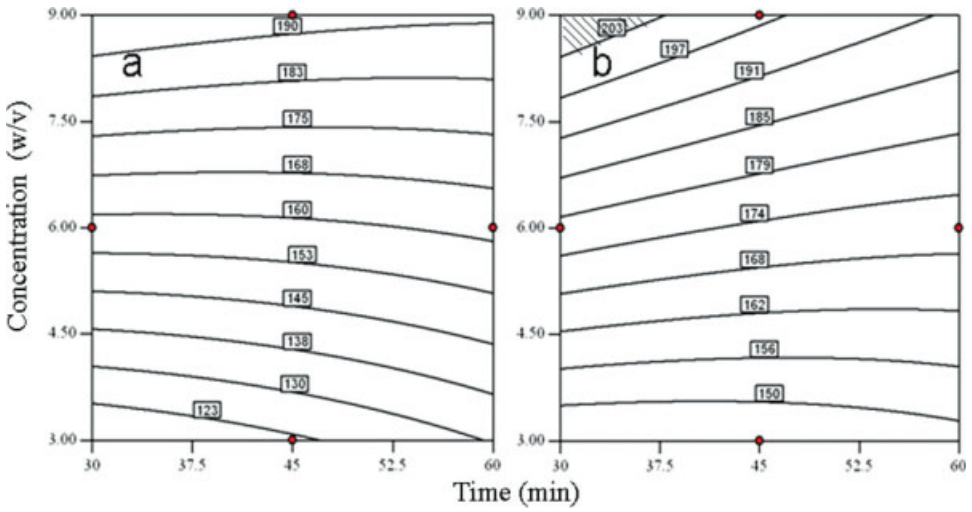

Figure 3 Effect of concentration and time on the water retention capacity (%) at various levels of temperature (a) 50°C and (b) 70°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed by other researchers and has attributed to the autocatalytic effect after certain time duration, thereby resulting in high weight loss.[2]

Effect of concentration and time

Figure 3 shows the contour plot of water retention capacity of the hydrolysed electrospun nanofibers at different concentration and time for constant temperature (at minimum and maximum levels). From the figures it can be seen that the water retention capacity increases with increase in concentration of the alkali used at both lower and higher temperatures. Moreover, it can be seen from the figures that the amount of water retained by electrospun membrane is higher at elevated temperature, indicating that hydrolysis of nitrile group into carboxyl group occurs at the elevated temperature, thereby increasing the water retention capacity. However, it should be noted that the effect of time is more pronounced at elevated temperature and can be seen by skew in the contour lines.

Effect of concentration and temperature

Figure 4 presents the effect of concentration and temperature on the water retention capacity of electrospun membranes. With increase in concentration and temperature there is an increase in water retention capacity of the membranes at both lower and higher time intervals but at higher time duration there is decrease in water retention capacity with

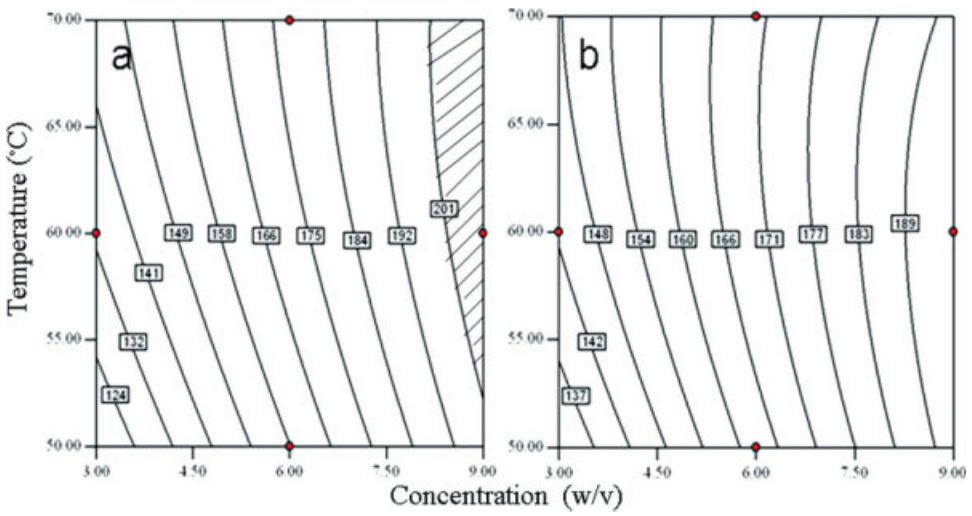

Figure 4 Effects of concentration and temperature on the water retention capacity (%) at various levels of time (a) 30 min and (b) 60 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

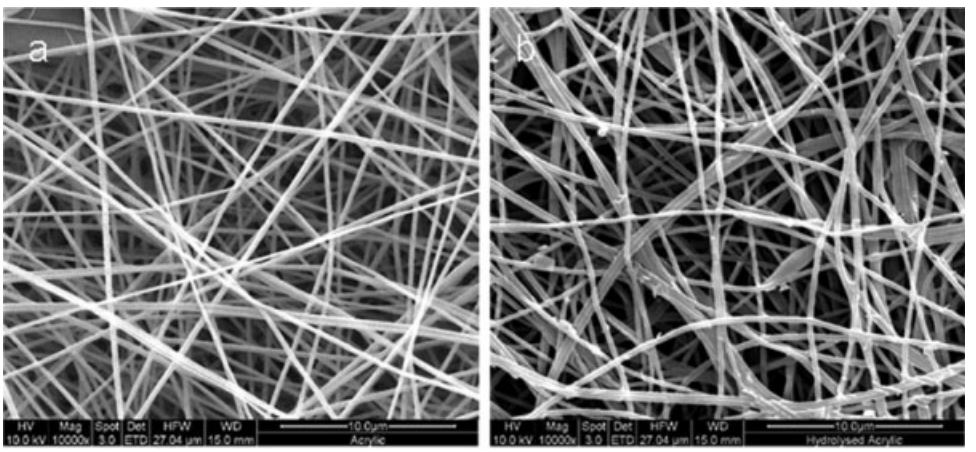

Figure 5 SEM photographs of (a) electrospun polyacrylonitrile nanofibres (b) hydrolyzed electrospun polyacrylonitrile nanofibres.

increase in alkali concentration as discussed earlier. Another interesting observation that occurred during the trials was that the specimens changed colour from pale yellow to dark red with increase in concentration and temperature. The appearance of color is due to polymerization thorough nitrile groups with the formation of chromophoric azopolyene structure which are subsequently hydrolysed by alkali with the formation of units containing amide and carboxyl groups.[16]

Characterization of the samples

SEM studies

The surface morphology of the electrospun polyacrylonitrile and hydrolysed fibres are presented in Figure 5. From the figure, it can be seen that the surface of the fibres has been altered as result of hydrolysis. In the case of parent electrospun sample the fibers are of uniform diameter and are closely packed with a smooth structure. With hydrolysis using alkali, the surface of the fiber has become non homogeneous and fiber swelling has also occurred. Moreover, lot of fibrils of fibers can be observed on the surface indicating the loosening of the chains due to hydrolysis. The fiber diameter and mean flow pore diameter of the electrospun polyacrylontrile fibers and the hydrolysed fibers shown in SEM images were 310 $\pm$ 50, 275 $\pm$ 75 nm, 0.9258 and 1.12 microns, respectively, indicating that there is a reduction in diameter and weight as hydrolysis occur.

FTIR spectroscopic analysis

The FTIR spectra of the starting acrylic material used to prepare the solution and the electrospun sample is given in Figures 6 and 7. From the Figure

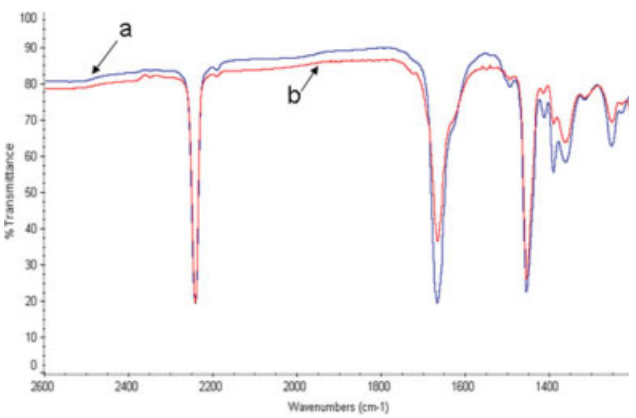

Figure 6 FTIR spectra of (a) starting acrylonitrile fibres (b) electrospun nanofibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

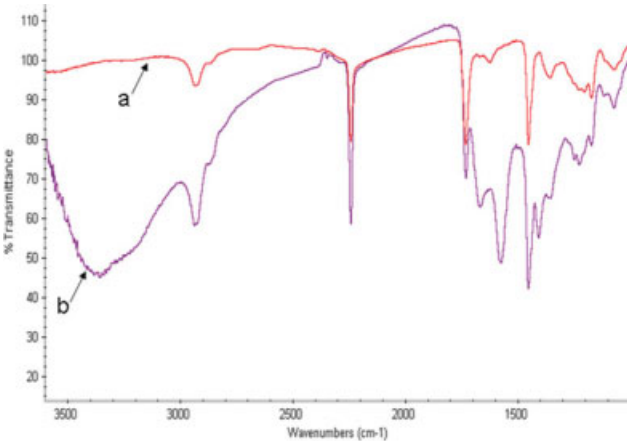

Figure 7 FTIR spectra of (a) electrospun polyacrylonitrile polymer (b) hydrolysed electrospun nanofibres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Weights Obtained in Training Artificial Neural Network

1st and 2nd layer	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}
	1.752	0.384	−1.544	0.139	0.786
	W_{21}	W_{22}	W_{23}	W_{24}	W_{25}
	−0.613	0.339	−0.949	1.150	−1.140
	W_{31}	W_{32}	W_{33}	W_{34}	W_{35}
	0.221	−0.088	−1.071	−0.531	−0.287
2nd and 3rd layer	W_{11}	W_{12}	W_{13}	W_{14}	W_{15}
	0.150	1.582	−1.034	−0.037	0.966
	W_{21}	W_{22}	W_{23}	W_{24}	W_{25}
	0.088	−0.294	−0.357	0.627	−1.061
	W_{31}	W_{32}	W_{33}	W_{34}	W_{35}
	1.034	1.316	−1.233	0.249	0.263
	W_{41}	W_{42}	W_{43}	W_{44}	W_{45}
	0.229	−1.159	0.893	0.539	−0.489
	W_{51}	W_{52}	W_{53}	W_{54}	W_{55}
	0.478	0.577	−1.013	0.594	0.708
3rd and 4th layer	W_{11}				
	−0.263				
	W_{21}				
	−1.801				
	W_{31}				
	1.036				
	W_{41}				
	−0.765				
	W_{51}				
	−1.588				

6, it can be clearly understood electrospinning has not altered the chemical integrity of the parent of sample. The hydrolysis of PAN electrospun fiber is evident from the FTIR-ATR of samples at different hydrolysis periods as shown in Figure 7. The electrospun polyacrylonitrile fiber shows a peak at 2245 cm^{-1} for the nitrile group and at 1740 cm^{-1} for the ester group. "In addition to that characteristic peaks for other groups are also present in the electrospun polyacrylontitrile fibre (γ OH), 2946 and 2874 cm^{-1} (γ C—H) asymmetric and symmetric in CH, CH_2, and CH_3 groups, 1457 cm^{-1} (δ CH_3 and δ $_S$ CH_2), 1363 cm^{-1} (δ CH_3 symmetric in CCH_3), 1172 cm^{-1} (γ C—N), 1074 cm^{-1}(δ C—N), where γ represents a stretching vibration, δ a blending vibration, δ_S a scissor vibration, and δ_τ a twisting vibration" as suggested in the literature.[27] After the hydrolysis with sodium hydroxide, a drastic change observed in the spectrum of the hydrolysed electrospun fibre. A broad adsorption band 3423 cm^{-1}, is observed which corresponds to the stretching vibration of the OH group and indicates the presence of OH groups in the hydrolysed electrospun fibres. The formation of peaks at 1573 and 1406 cm^{-1} wave numbers indicate the existence of imine (—C=N—) conjugated sequences in the modified fiber.[13,20] It should also be noted that the presence of peak at 2245 cm^{-1} in the hydrolysed fibre indicates that the part of the nitrile group in the parent sample is hydrolyzed.

Comparison between ANN and empirical model

The ANN was trained upto 75,000 cycles to obtain optimum weights. The weights of ANN for water retention capacity are given in Table V. Tables IV and VI gives the experimental values, predicted values and the prediction error for the water retention capacity of hydrolyses electrospun nanofibrous membrane. Both statistical model and ANN model shows a very good relationship (R^2) between the experimental and predicted response values. The empirical model shows much lower absolute percentage error than the ANN model. This could be due to the fact that the response is linear and it has been known that the prediction by ANN model is very accurate when more amount of data is fed for training to simulate the actual experimental conditions. However, it should be noted that both the models have an error percentage less than 2% indicating the reliability of the model developed.

CONCLUSIONS

Electrospun nanofibrous membrane fiber diameter in the range of 310 ± 50 nm were prepared to study the water retention capacity of the membranes under different hydrolyzing conditions. Water retention capacity of the electrospun membranes was found to increase with alkali concentration, temperature and time. The results of FTIR and SEM images confirms that the surface modification of the fibres takes place due to hydrolysis and thereby making it a good choice for various water absorbent applications. Moreover, the results indicates that ANN coupled with empirical model can be a handy tool in predicting the outcome of hydrolysis of electrospun membrane.

TABLE VI
Experimental Verification of Predicted Results

	Variables			Water retention capacity (%)			Absolute error (%)	
					Predicted			
Trial no.	X_1	X_2	X_3	Experimental	Empirical	ANN	Empirical	ANN
1	7	55	30	178	176	174	1.12	2.24
2	4	65	50	150	152	152	1.30	1.33
3	5	75	15	172	169	171	2.31	1.15

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References

1. Fischer-Colbrie, G.; Matama, T.; Heumann, S.; Martinkova, L.; Paulo, A. C.; Guebitz, G. J Biotechnol 2007, 129, 62.
2. Gupta, M. L.; Gupta, B.; Oppermann, W.; Hardtmann, G. J Appl Polym Sci 2004, 91, 3127.
3. Reneker, D. H.; Yarin, A. L. Polymer 2008, 49, 2387.
4. Lala, N. L.; Ramaseshan, R.; Bojun, L.; Sundarrajan, S.; Barhate, R. S.; Ying-jun, L.; Ramakrishna, S. Biotechnol Bioeng 2007, 97, 1357.
5. Venugopal, J.; Vadgama, P.; Sampath Kumar, T. S.; Ramakrishna, S. Nanotechnology 2007, 18, 055101.
6. Venugopal, J.; Low, S.; Choon, A. T.; Kumar, A. B.; Ramakrishna, S. Artif Organs 2008, 32, 388.
7. Ma, Z.; Ramakrishna, S. J Membr Sci 2008, 319, 23.
8. Ramakrishnan, R.; Ramakrishna, S. J Am Ceram Soc 2007, 6, 1836.
9. Kim, S.; Lim, S. K. Appl Catal B 2008, 84, 16.
10. Sun, J. I.; Kwon, O.; Kim, Y. H.; Park, S. J.; Le, Y. S. Microporous Mesoporous Mater 2008, 115, 514.
11. Yoon, K.; Kim, K.; Wang, X.; Fang, D.; Hsiao, B. S.; Chu, B. Polymer 2006, 47, 2434.
12. Sun, J. I.; Kim, M.; Lee, Y. S. Mater Lett 2008, 62, 3652.
13. Oh, G. Y.; Ju, Y. W.; Kim, M. Y.; Jung, H. R.; Kim, H. J.; Lee, W. J. Sci Total Environ 2008, 393, 341.
14. Saeed, K.; Haider, S.; Oh, T. J.; Park, S. Y. J Membr Sci 2008, 322, 400.
15. Wang, Y.; Yang, O.; Shan, G.; Wang, C.; Du, J.; Wang, S.; Li, Y.; Chen, X.; Jing, X.; Wei, Y. Mater Lett 2005, 59, 3046.
16. Anli, O. Eur Polym J 1990, 26, 9.
17. Choi, H. M. J Appl Polym Sci 2007, 105, 853.
18. Liu, H.; Hsieh, Y. L. Macromol Rapid Commun 2006, 27, 142.
19. Box, G. E. P.; Hunter, J. S. Ann Math Stat 1954, 28, 195.
20. Cochran, W. G.; Cox, D. W.Experimental Design; Wiley: New York, 1968.
21. Meyers, R. H.; Montgomery, D. C.Response Surface Methodology: Process and Product Optimization Using Design of Experiments; Wiley: 1995.
22. Montgomery, D. C.Design and Analysis of Experiments; Wiley: New York, 1997.
23. Annadurai, G.; Sheeja, A. Y. Bioprocess Eng 1998, 18, 463.
24. Senthil kumar, M.; Selvakumar, N. Dyes Pigments 2006, 68, 89.
25. Hinton, G. E. Sci Am 1992, 267, 145.
26. Senthilkumar, M. Dyes Pigments 2007, 75, 356.
27. Deng, S.; Bai, R.; Chen, J. P. J Colloid Interface Sci 2003, 260, 265.