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MATHEMATICAL MODELLING OF THE ELECTROSPINNING PROCESS FOR PRODUCTION OF POLYVINYL ALCOHOL NANOFIBERS

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ABSTRACT. The process parameters were studied during the fabrication of polyvinyl-alcohol (PVA) nanofibers via electrospinning. The factorial experiment design model described electrospinning as an efficient, versatile approach for fabricating nanofibers. The mathematical model was developed by considering the effect of voltage, concentration, the distance between the pin and the collector, and flow rate, respectively. The influence of these parameters on the diameter and morphology of obtained PVA fibers was investigated by transmission electron microscopy (TEM). It was found that the concentration had the most significant influence on the polymer fiber diameter.

Keywords: *electrospinning, process parameter, polyvinyl alcohol, response surface method, average fiber diameter*

INTRODUCTION

Electrospinning is a fast, efficient, and cheap way to produce polymer fibers in the micro, and nanometer range [1,2]. Briefly, electrospinning is based on the flow of the polymer solution through a needle under a field of electrostatic forces. During the process, most of the solution evaporates, and the polymer fiber accumulates on the sample collection surface, leading to a random two-dimensional fiber network [3]. Depending on the polymer type, the resulting structure may possess improved physical properties such as smaller pore size, higher porosity, higher surface-area-to-volume ratio and three-dimensional features [1-3]. The structural properties also depend on the

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experimental conditions: concentration, applied voltage, needle to collector distance, flow rate, etc. [4-6]. Different polymers require individual process parameters optimization. In this regard, the response surface methodology (RSM) method was applied for chitosan-collagen nanofibers, using a sequence of designed experiments to obtain an optimal response [7]. The key parameters for the electrospinning process of PVA are the concentration of polyvinyl alcohol (PVA) solution, voltage applied, distance between the needle and collector, and flow rate [8-11].

PVA is a water-soluble, hydrophilic, non-toxic, and biocompatible polymer with good chemical and mechanical properties and widely used in creating hydroxyapatite matrixes, removing heavy metals' ions, drug carriers, tissue engineering, various intelligent materials, wound dressings, bone regeneration [12]. Elkasaby et al. optimized the production of PVA nanofibers using ANOVA and the Taguchi orthogonal array L27OA method. The PVA solution was prepared at a higher temperature of 70 ^{o}C and short mixing time [13]. The effects of five factors, namely applied voltage, concentration, collecting distance, flow rate and rotational speed, were also investigated [13]. For the investigation and optimization of the process, the design of experiment (DOE) is a suitable tool due to the excellent description of the investigated process and low number of experiments [14].

Usually, the experimental design has been done by studying one variable (factor) at a time. This approach is based on the incorrect assumption that the factors do not affect one another. The one variable at a time (OVAT) approach has certain disadvantages: many experiments are needed; the information is only available in the points studied; the interactions between factors cannot be observed, leading to the incorrect interpretation of the results; the researcher may find an acceptable response, but the chance of finding the global optimum is slight [15]. To eliminate these problems, the multivariate statistical approach named design of experiment (DOE) was introduced. This method is the most appropriate to determine the factor's individual and combined effects, as well as their optimal points. The DOE methods' minimum and maximum level for each factor must be defined. It is helpful to place these levels on a coded scale (usually between -1 and +1) better to understand the significance of the factors and their interactions. It is recommended to perform the experiments in a randomized order to minimize the effects of unwanted factors. The experimental range of an analytical problem usually contains minima, maxima, and saddle points; hence, quadratic terms must be introduced to get an appropriate description. To estimate these terms, each factor must be assigned at least three levels.

One of the most used approaches is central composite design (CCD) [14,16]. CCD is the extension of the whole or fractional factorial design. These consist of N experiments, divided into the following categories: (a) Factorial points – the coded value of each factor is -1 or +1. These can be used to estimate the main and two-factor interactions. This part is technically a two-level full or fractional factorial design with 2^{k-m} data points, where k is the number of factors, and m is the number of applied fractions; (b) Axial points – in this part, one factor's coordinate is +α or –α, and all the other factors get their center point. The number of experiments in this part is 2^k; (c) Center points – in this part, every factor is assigned its center value. These experiments are used to estimate the experimental error and determine the quadratic terms. This study used the CCD method to correlate the process factors and the average diameter of PVA nanofiber obtained by electrospinning.

RESULTS AND DISCUSSION

Determination of fiber diameter

For every sample 10 TEM images were taken, from which around 100 segments were analyzed. It was clearly observed that the fiber diameter of the final product depends on the parameters used in the synthesis procedure. The low average diameter was 0.0749 μm for run 9 (Figure 1a) and the largest average diameter was 0.3096 μm for run 5 (Figure 1b).

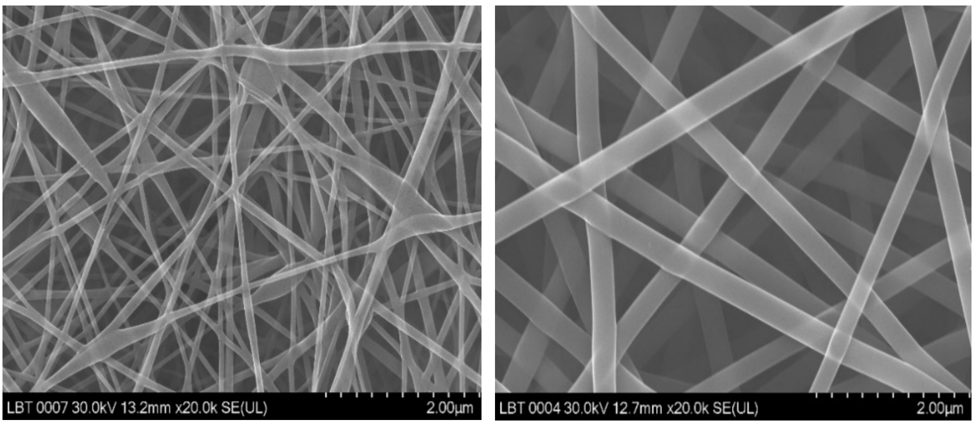

Figure 1. TEM image of the experimental runs (a) 9 and (b) 5

Estimation of coefficients in a mathematical polynomial function

After performing the experiments to obtain outputs according to the experimental design, the next step considered the vector of variables (c, U, I, q) and corresponding response (diameter). The typical response surface function for four inputs is in the form of the following equation:

$$\begin{aligned}\mathrm{Y(response)} = {} & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5x_1x_1 + b_6x_2x_2 + b_7x_3x_3 \\ & + b_8x_4x_4 + b_9x_1x_2 + b_{10}x_1x_3 + b_{11}x_1x_4 + b_{12}x_2x_3 + b_{13}x_2x_4 \\ & + b_{14}x_3x_4\end{aligned}$$

where x_n is the corresponding factor and b_n is the coefficient, Y is the response, in our case the nanofiber diameter. Using multiple linear regression analysis on data obtained from experimental results, the following model was deduced:

$$\begin{aligned}d(\mu m) = {} & -0.166 + 0.0552 * c + 0.1179U - 0.2844 * I + 0.000954 * q - 0.00282 * c^2 \\ & - 0.00224 * U^2 + 0.01414 * I^2 - 0.000001 * q^2 - 0.000812 * c * U \\ & + 0.00417 * c * I + 0.000004 * c * q - 0.001917 * U * I + 0.000006 \\ & * U * q - 0.0000241 * I * q\end{aligned}$$

The correlation coefficient (R2) checked the efficiency of the correlated model. In the obtained model this coefficient value is 97.25%, which indicated that the model does not explain only 2.75% of the total variations. The value of adjusted R^2 is 94.68% is also high to advocate the significance of the model.

The goodness of fit was also characterized by ANOVA analysis (Table 1). The Fisher F-test with a very low probability value (P-value) demonstrates a high significance for the regression model.

The Pareto charts (Figure 2) reproduced from ANOVA results were used to visualize the main effects and their interactions. According to the results concentration (c), square of the distance (I^2), the interaction between concentration and distance (c*I), the square of flow rate(q^2) were found to be significant at 95% confidence level.

Factorial plots were obtained using the regression equation. One factor was varied, and all others remained constant at a specific value, usually their center point. Figure 3 shows the individual effect of the given factor on the response. Based on the obtained results, we can conclude that the flow rate is most affected by the other parameters.

Table 1. Analysis of variance ANOVA for central composite design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	0.133014	0.009501	37.89	0.000
Linear	4	0.120722	0.030180	120.37	0.000
c	1	0.118325	0.118325	471.94	0.000
U	1	0.000066	0.000066	0.26	0.615
l	1	0.002006	0.002006	8.00	0.013
q	1	0.000325	0.000325	1.30	0.273
Square	4	0.007394	0.001848	7.37	0.002
c*c	1	0.000336	0.000336	1.34	0.265
U*U	1	0.001051	0.001051	4.19	0.059
l*l	1	0.002622	0.002622	10.46	0.006
q*q	1	0.001573	0.001573	6.27	0.024
2-Way Interaction	6	0.004899	0.000816	3.26	0.030
c*U	1	0.000380	0.000380	1.52	0.237
c*l	1	0.002500	0.002500	9.97	0.007
c*q	1	0.000033	0.000033	0.13	0.722
U*l	1	0.001190	0.001190	4.75	0.046
U*q	1	0.000148	0.000148	0.59	0.455
l*q	1	0.000648	0.000648	2.58	0.129
Error	15	0.003761	0.000251		
Lack-of-Fit	10	0.002587	0.000259	1.10	0.487
Pure Error	5	0.001174	0.000235		
Total	29	0.136775			

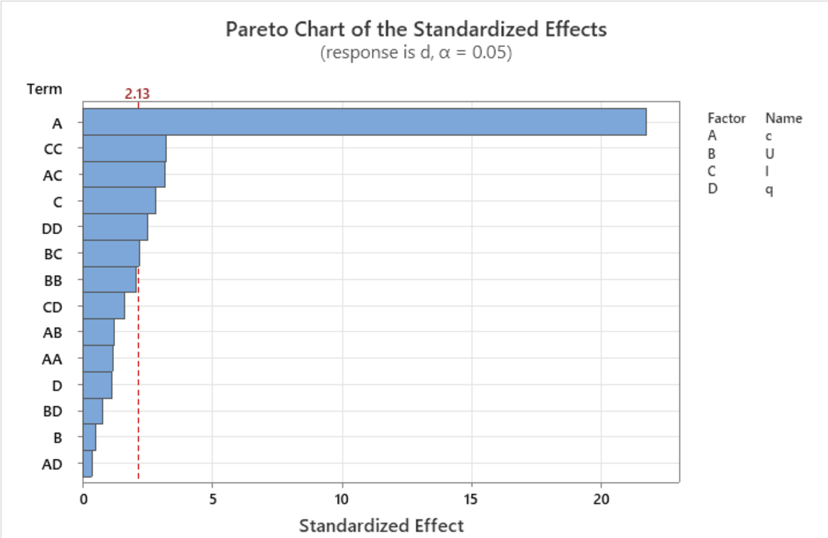

Figure 2. Pareto chart of the standardized factors

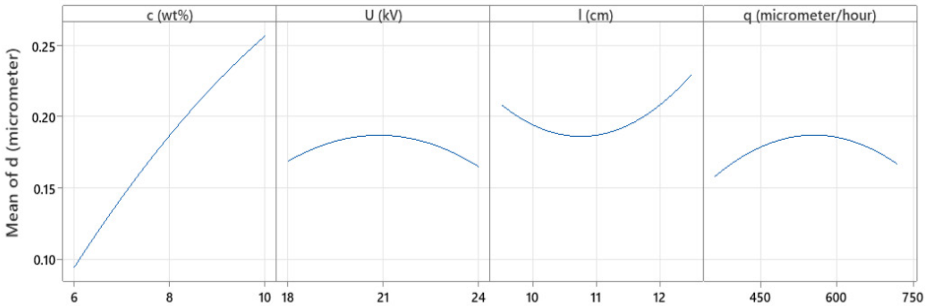

Figure 3. Factorial plot for the diameter vs. the parameters (c, U, l, q)

Response surface plots

The central composite design (CCD) results were used to generate response surfaces. The predicted values of the fiber diameters (d) calculated from the mathematical model were plotted against the factors as a response surface plot, a theoretical three-dimensional scheme to visually explain the relationship between the response and independent variables.

From the surface plots we can conclude that: (*i*) the concentration has the greatest effect on the fiber diameter and (*ii*) the concentration change in combination with the change of voltage, distance or flow rate causes the fiber diameter to behave non-linearly, which also indicates the interaction of the concentration with the other parameters. According to Figure 4, the effect of any other parameters except concentration is significantly smaller. Also, their interactions are weaker.

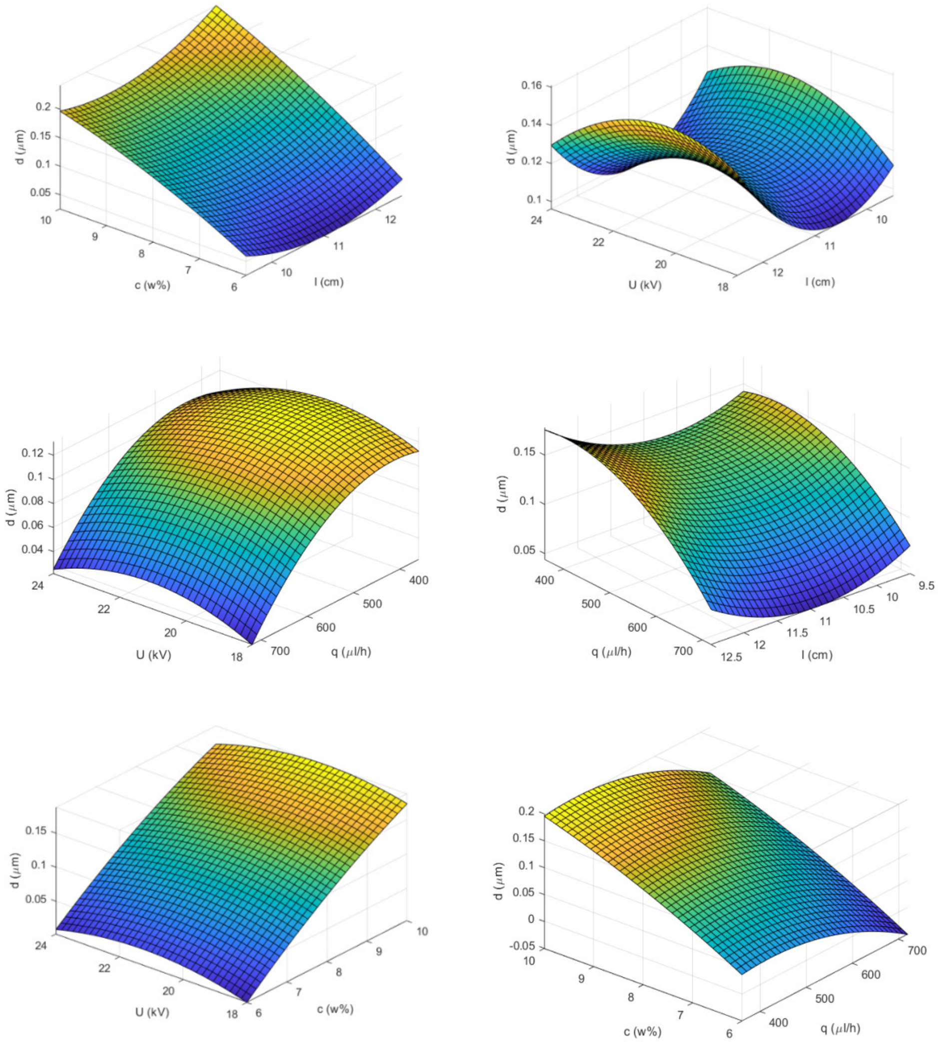

Figure 4. Surface plot of Diameter (d) vs. the factors: Plot of d vs. c, l; Plot of d vs. l, U; Plot of d vs. q, U; Plot of d vs. q, l; Plot of d vs. c, U; Plot of d vs. c, q

Response optimization

After checking the accuracy of the model, the optimal conditions are determined. Based on the obtained model, the level of each factor to get the optimal response signal was determined using Minitab software.

Table 2. Optimal levels of the factors

c (%wt)	U (kV)	L (cm)	q (μL/h)	Calculated fiber average diameters (μm)
6	18	10.7	360	0.046

CONCLUSIONS

Response surface method was used to optimize the production of PVA nanofibers by electrospinning. The resulting mathematical model can describe and predict the effect of the following factors: concentration, distance, voltage, and flow rate. Of the studied parameters, the concentration was found to have the most significant influence on the fiber diameter. The interaction between and individually of the other parameters is low and does not affect the diameter significantly. The appropriate diameter can be reached only by choosing the appropriate concentration.

EXPERIMENTAL SECTION

Materials, apparatus, and software

Hight purity PVA (>99.5%) with a molecular weight of ≈130 g/mol was purchased from Sigma-Aldrich. Distilled water was used as solvent in the preparation steps. Bionicia electrospinning system FLUIDNATEK 2017-F012 was used during the experiments. The fibers were investigated with Hitachi SU8230 (Tokyo, Japan) microscope, and the ImageJ software was used to interpret images. The regression analysis of experimental data was explored using the Minitab 19 and MATLAB 2018 software.

Design of experiment

Experimental design has three defining steps: performing statistically constructed experiments, estimating the mathematical model coefficients, and verifying the model. The goal is to write a mathematical equation that includes the effect of the studied parameters on fiber thickness and morphology.

The studied factors were PVA solution concentration (c), applied voltage (U), collector distance from the needle (l), and flow rate (q), where the levels of the studied parameters are shown in Table 3.

Table 3. The variables and their levels for the full factorial experimental design

Factor	Name	Units	Min	Max
c	Concentration	%wt	6.00	10.0
U	Voltage	kV	18.0	24.0
l	Distance	cm	9.50	12.50
q	Flow rate	μL/h	360	720

Elkasaby et al. tested the first three factors in a broader range, and the flow rate was set to a lower value (100-300 μL/h) compared to 360-720 μL/h used in this study. Accordingly, there are significant differences in the obtained fiber size, the obtained values of 0.0749 and 0.31, comparing to 0.51 and 1.87 obtained by Elkasaby et al. The authors also created two models, with the help of which they tried to predict the system's behavior. The correctness of the obtained model was verified using the average model accuracy (AMA) calculated from residuals, which in the case of the first model is 84.3%. In contrast, in the case of the second model is approximately 80%. In our case, this value is 94.0%. Despite the differences, similar conclusions were reached based on which solution concentration affects fiber size [17].

The coded and the real values of the factors are presented in Table 4.

Table 4. Explanation of the code system

Factor	Name	Units	-1	0	1
c	Concentration	%wt	6.00	8.00	10.0
U	Voltage	kV	18	21	24
l	Distance	cm	9.50	11	12.5
q	Flow rate	μL/h	360	540	720

The levels of the factors are selected based on the size of the experimental range, the error in the factor fixation and the choice of the variation interval. After determining the experimental design depending on the number of factors and the nature and magnitude of their influence, the mathematical model can be selected. The coefficients show the strength of each factor and interaction; their values express how much the response characteristic change when the given factor changes [18,19].

In order to determine the effect of the above-mentioned factors, the response surface method with a central composite design was applied. The data set was composed of 30 experiments for each of the responses collected, as it is shown in Table 5.

Table 5. Central composite design and the fiber average diameters for each experimental run

	Coded values of the factors				Fiber average diameters (μm)
Run	c(%wt)	U(kV)	l(cm)	q (μL/h)	d
1	1	-1	-1	-1	0.1945
2	1	-1	-1	1	0.2294
3	1	1	-1	-1	0.2082
4	1	1	-1	1	0.2445
5	1	-1	1	-1	0.3096
6	1	-1	1	1	0.2655
7	1	1	1	-1	0.2396
8	1	1	1	1	0.2480
9	-1	-1	1	-1	0.0749
10	-1	1	1	-1	0.0798
11	-1	-1	1	1	0.0848
12	-1	1	1	1	0.0787
13	-1	-1	-1	-1	0.0784
14	-1	1	-1	-1	0.0858
15	-1	-1	-1	1	0.0774
16	-1	1	-1	1	0.0905
17	1	0	0	0	0.2656
18	-1	0	0	0	0.0952
19	0	1	0	0	0.1741
20	0	-1	0	0	0.1692
21	0	0	1	0	0.2325
22	0	0	-1	0	0.2147
23	0	0	0	1	0.1814
24	0	0	0	-1	0.1529
25	0	0	0	0	0.1697
26	0	0	0	0	0.2077
27	0	0	0	0	0.1873
28	0	0	0	0	0.1871
29	0	0	0	0	0.1680
30	0	0	0	0	0.1714

The experiments were established according to Table 5.

Preparation of PVA solution and electrospinning process

The appropriate amount of PVA was dissolved in distilled water in an ultrasonic bath, stirred 6 h at 60 ℃, and then 24 h at ambient temperature. The resulting solution was introduced to the electrospinning device's syringe comprising a programable pump that ensures a specific flow rate. The collector was adjusted to the chosen distance and was covered with aluminum foil, where the PVA fibers were collected. The voltage and flow rate were adjusted via a microcontroller over a range of values suitable for most electrospinning. The electrospinning process was carried out at room temperature.

Characterization of prepared PVA fiber samples

The morphology of samples was investigated by transmission electron microscopy (TEM) and the resulting images were analyzed using the ImageJ software package (Version 1.51) with DiameterJ plugin.

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REFERENCES

1. A. Frenot. I.S. Chronakis, Curr. *Colloid. Interface. Sci.,* **2003**, *8*, 64-75
2. D. Li., W.Y. Xia, *Adv. Mater.* **2004**, *16*, 1151-1170
3. Joseph, Deitzel. James D, Kleinmeyer. Donovan, Harris. Nora C, Beck-Tan. *Polymer,* **2001**, *42*, 261-272
4. Z. Li., C. Wang. *One-Dimensional nanostructures. Springer Briefs in Materials*. Springer, Berlin, Heidelberg. **2013**. pp. 15-28
5. C.J. Thompson, G.G. Chase, A.L. Yarin, D.H. Reneker. *Polymer*, **2007**, *48*, 6913-6922
6. Y. Meyva-Zeybek, C. Kaynak, *J. Appl. Polym. Sci.*, **2020**, *138*, 3
7. N. Amiri, A. Moradi, S.A.A. Tabasi, J. Movaffagh, *Mater. Express*, **2018**, *5*, 4
8. A.K. Aljehani, M.A. Hussaini, M.A. Hussain, N.S. Alothmany, R.W. Aldhaheri, 2nd Middle East Conference on Biomedical Engineering, Doha, **2014**, 379-381

9. S.F. Dehghan, F. Golbabaei, B. Maddah, M. Latifi, H. Pezeshk, M. Hasanzadeh, *J. Air Waste. Manage.*, **2016**, *66*, 912-921
10. N.J. Kanu, E. Gupta, U.K. Vates, G. Singh, *Mater.Express*, **2020**, *7*, 3
11. R.-R. Yang, J.-H. He, L. Xu, J.-Y. Yu, *Mater. Sci. Tech-Lond*., **2010**, 26, 1313-1316
12. S. Ullah, M. Hashmi, N. Hussain, A. Ullah, M.N. Sarwar, Y. Saito, S.H. Kim, I.S. Kim, *J. Water Process. Eng.*, **2020**, *33*, 101-111
13. M. Elkasaby, H.A. Hegab, A. Mohany, G.M. Rixvi, *Adv. Polym. Tech.*, 2018, *37*, 2114-2122
14. X. Ji, J. Guo, F. Guan, Y. Liu, Q. Yang, X. Zhang, Y. Xu, *Gels*, **2021**, *7*, 223
15. S.S. Nasrollahi, Y. Yamini, A. Mani-Varnosfaderani, *J. Food Compos. Anal.*, 2022, *106*, 104339
16. Q. Zhang, T.M. Young, D.P. Harper, T. Liles, S. Wang, *Carbohyd. Polym.* **2021**, *2*, 100120
17. M. Elkasaby, H.A. Hegab, A. Mohany, G.M. Rizvi, *Adv. Polym. Tech*., **2017**, 37, 1-9
18. George E.P. Box, J. Stuart Hunter, William G. Hunter, Statistics for Experimenters: Design, Innovation, and Discovery, 2nd Edition, Wiley, **2005**
19. M.A. Badawi, L.K. El-Khordagui, *Eur. J. Pharm. Sci.* **2014**, *58*, 44-54