https://doi.org/10.30799/jacs.204.19050103 J. Adv. Chem. Sci. – Volume 5 Issue 1 (2019) 615–617

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ISSN: 2394-5311

Study on Production and Kinetics of Chitosan from Shrimp Shell Waste using Factorial Design Experimental Technique

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ARTICLE DETAILS

Article history:
Received 06 February 2019
Accepted 21 February 2019
Available online 15 March 2019

Keywords:
Chitosan
Shrimp Shells
Factorial Design

ABSTRACT

In order to deduce the optimum conditions of chitosan production, a statistical model based on 2^3 full factorial design was used. The optimum conditions of deacetylation reaction were investigated using batch experiments technique. The investigated factors are NaOH concentration, time of the deacetylation reaction, and reaction temperature. A first order model was elaborated and a regression equation obtained that showed a strong determination coefficient (0.946). The kinetics of the reaction was studied and the order of deacetylation reaction was deduced and was found to be pseudo – first order law. Activation energy of the deacetylation reaction was found to be 3.86 kJ/mole.

1. Introduction

Chitosan is a natural polymer with considerable properties. Some of these properties are is bioreactivity, biocompatibility and biodegradability. It is produced by partial deacetylation of chitin, which found naturally in the exoskeletons of insects, shells of crustaceans, and fungal cell walls [1, 2]. Its properties promote the application in many fields such as food industry as antimicrobial film to cover fresh fruits and vegetables [3, 4], bio medicals [5], and water treatment [6].

Types of chitosan polymer are synthetic and natural. Natural chitosan has been extracted from crustacean shells, which contain chitin, $CaCO_3$, proteins, lipids and pigments [7,8]. The extraction process is achieved in three steps – deproteination, demineralization and lipids and pigments removal [2].

The most utilized methods to convert Chitin into chitosan are by enzymatic means or alkali deacetylation, [9]. During the deacetylation reaction, part of polymer N-acetyl links are broken. It results in the formation of D-glucosamine units, which contain a free amine group. This increases the polymer's solubility in aqueous acidic solution and this occurs approximately at 50 % degree of deacetylation (DDA) [10, 11].

Most of the physical, mechanical and chemical properties of this biopolymer significantly depend on the DDA. For example, chitosan with a higher DDA represents higher antimicrobial activity [12]. The DDA of chitosan depends on the source, preparation method, and the reversal of the process steps [13, 14].

Naznin [15] stated that the optimum conditions for chitosan production from shrimp shell in Bangladesh were observed at using 30% HCl for demineralization, 1.5 N NaOH for deproteinization, 50% NaOH for deacetylation and resulted in chitosan yield of 8.7%. Weska et al. [9] studied deacetylation stage in the production of chitosan from shrimp wastes using the response surface methodology, and the optimum condition for the deacetylation was observed with 45% NaOH at a temperature of 130 °C and in 90 min and corresponded to a molecular weight of chitosan of about150 kilodalton (kDa) and a deacetylation degree of 90%. Hossain and Iqbal [16] performed demineralization with 3% HCl for 16 h, deproteinization with 4% NaOH for 20 h, and deacetylation with 60% NaOH for 24 h at 60 °C and resulted in the DDA of 81.24%.

The present work aims to determine the optimum conditions for deacetylation stage in the production of chitosan from shrimp wastes using full factorial design experimental technique having as variables NaOH concentration, temperature and time of reaction.

2. Experimental Methods

2.1 Raw Materials

The raw materials used in this study were shrimp shells collected from domestic use, hydrochloric acid (37%) analytical grade, and sodium hydroxide supplied by El-Gomhoreya Co., Cairo, Egypt.

2.2 Chitosan Production

Shrimp shells were dried and ground in a ball mill, then screened and only the fraction of 0.6 mm particle size was used. Deproteinization was performed using 3.5% NaOH solution for 2 h at 60 °C. Demineralization was performed by soaking in 1 N HCl solution for 1 h at 25 °C during this step calcium carbonate is transformed into calcium chloride. Then deacetylation was performed to produce chitosan as shown in the following Fig. 1.

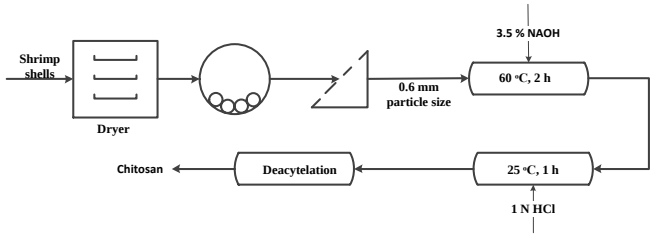

Fig. 1 Simplified flow chart of the experimental procedure

2.3 Degree of Deacetylation

During the deacetylation step the effects of sodium hydroxide concentration, temperature, and time were studied. The degree of deacetylation (DD) was detected using FTIR to find the depth of the peak and then substituting in equation (1) using the baselines proposed by Domszy and Roberts [17],

$$\%DD = (100 - \left(\frac{A_{1660cm-1}/A_{3450cm-1}}{1.33}\right)) * 100 \quad (1)$$

Where: $A_{1660\ cm-1}$: The depth of the peak at 1660 cm^{-1}
$A_{3450\ cm-1}$: The depth of the peak at 3450 cm^{-1}

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https://doi.org/10.30799/jacs.204.19050103

Cite this Article as: E.F. Abadir, N.F. Abdel Salam, F.I. Barakat, Study on production and kinetics of chitosan from shrimp shell waste using factorial design experimental technique, J. Adv. Chem. Sci. 5(1) (2019) 615–617.

2.4 Experimental Design

The kinetics of the deacetylation reaction was also studied. The rate of deacetylation reaction was assumed to be proportional to the concentration of acetamide group. The effect of the concentration of sodium hydroxide was studied in the range of 40 – 50%, the temperature varied from 60 to 80 °C and the treatment time varied from 2 to 5 h as shown in Table 1.

The application of orthogonal factorial design technique involves the following steps [18, 19]. Each of the three aforementioned variables was set at two levels. Table 1 shows the chosen values. The choice was made according to from literature data [2, 8, 9]

Table 1 Experimental ranges of investigated independent variables

Variable	Symbol	Unit	Min. value	Central value	Max. value
NaOH Conc.	C	Wt.%	40	45	50
Temperature	T	°C	60	70	80
Time	t	h	2	3.5	5

Coded variables are next defined for each of the three-parameter investigated so as to obtain – 1, +1 or 0 values for minimum, central, and maximum levels respectively.

A design matrix M is then established involving 2^3 combinations of –1, and +1 values of the 3 variables. The degree of deacetylation (DD) for all 8 experimental conditions is then measured, and a column vector Y (conversion) is obtained. In first order design the regression equation for coded variables takes the form,

$$y = a_0 + \sum_{i=1}^{5} a_i x_i + \sum_{i=1,j=1,i\neq j}^{5} a_{ij} x_i x_j + \sum_{i\neq j\neq k}^{5} a_{ijk} x_i x_j x_k + \sum_{i\neq j\neq k\neq l}^{5} a_{ijkl} x_i x_j x_k x_l + a_{12345} x_1 x_2 x_3 x_4 x_5 \quad (2)$$

This equation contains 8 constants corresponding to the coefficient column vector A. The value of the coefficients of A can be obtained from the equation,

$$A = M^{-1}Y \quad (3)$$

Upon performing 11 experimental runs at the conditions specified in Table 2 and the three replicates at the centre point of design, the values of the coefficients in the coded regression Eq.(2) could then be obtained by applying Eq.(3).

3. Results and Discussion

After applying the t – test, some of the coefficients are eliminated for being statistically insignificant, and the coded variables then replaced by original variables, hence the regression equation will have the following form,

$$Y = 57.05 + 2.775X_1 + 2.8X_2 + 26.05X_3 \quad (4)$$

Once the regression equation has been established and non-significant coefficients are eliminated, the validity of the expression can be tested by calculating the determination coefficient R^2. R^2 was found to be 0.946, meaning that 94.6% of the variation in conversion is due to the variations in the three parameters. On the other hand, 5.4% of the variation in conversion is due to other reasons, such as experimental errors or any other factors not considered.

Table 2 Design conditions, and observed degree of deacetylation (first order model)

Run	t	X_1	T	X_2	C	X_3	Y (observed)
1	2	-1	60	-1	40	-1	30
2	2	-1	60	-1	50	+1	84.1
3	2	-1	80	+1	40	-1	25
4	2	-1	80	+1	50	+1	78
5	5	+1	60	-1	40	-1	36
6	5	+1	60	-1	50	+1	89.3
7	5	+1	80	+1	40	-1	33
8	5	+1	80	+1	50	+1	81
9	3.5	0	70	0	45	0	51.5
10	3.5	0	70	0	45	0	53.2
11	3.5	0	70	0	45	0	55.1

The observed conversions can be compared with the conversions calculated from the deduced regression equation. The results can be summarized in Fig. 2.

3.1 Effects of Investigated Parameters on DD%

From the deduced equation, it is clear that the three parameters have positive impact on the degree of deacetylation, and that there is no interaction between the three parameters.

From the equation it can be deduced that, the concentration of sodium hydroxide has the highest impact on the degree of deacetylation as shown in Fig. 3. It is clear that increasing the concentration from 40 to 50%, increases the degree of deacetylation from 25.4 to 77.5% at 2 h.

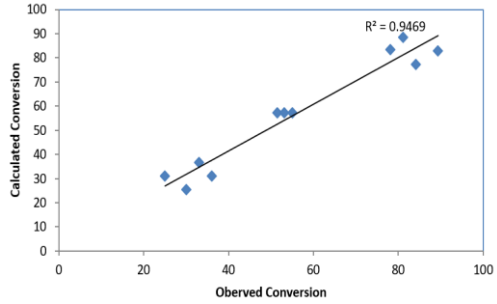

Fig. 2 Observed conversion versus calculated conversion

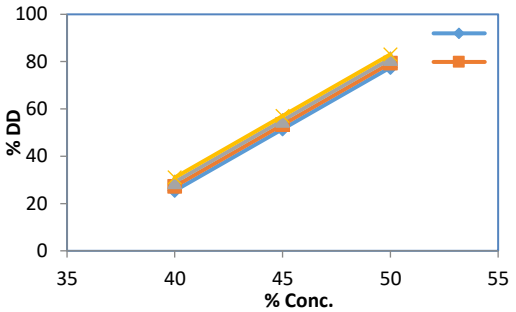

Fig. 3 Effect of NaOH concentration on the degree of deacetylation at 60 °C

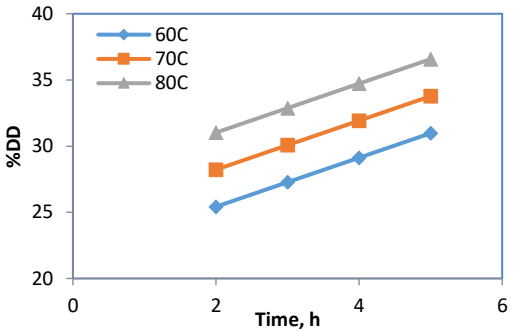

Fig. 4 Effect of treatment time on the degree of deacetylation at 40% NaOH

The effect of treatment time on the degree of deacetylation can be shown in Fig. 4. It is clear that the impact of treatment time on the degree of deacetylation is less than the effect of sodium hydroxide concentration. It also can be deduced that the process of deacetylation is an endothermic process as the degree of deacetylation increases by increasing the temperature from 60 to 80 °C. To study the reaction kinetics, –ln (1-DD) was plotted *vs.* t. It was found that the reaction follows the pseudo – first order law as shown in Fig. 5.

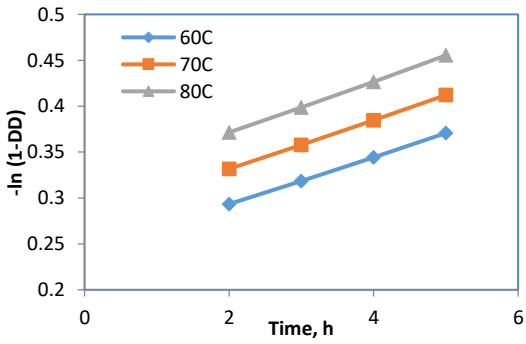

Fig. 5 Plot of –ln (1-DD) *Vs.* t

https://doi.org/10.30799/jacs.204.19050103

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3.2 Reaction Kinetics

The reaction rate constant can be calculated from the slope of –ln(1-DD) *vs.* t. The effect of temperature on reaction rate constant is shown in Fig. 6.

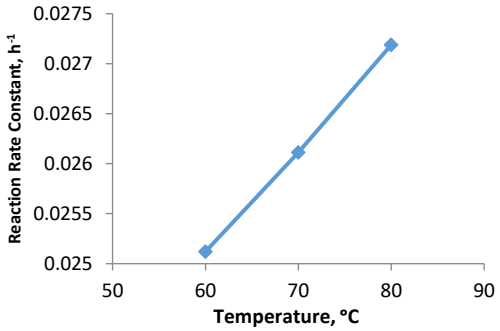

Fig. 6 Effect of temperature on the reaction rate constant at 40% NaOH

As the deacetylation process is an endothermic process, the reaction rate constant is increased by increasing the reaction temperature. By plotting ln K *vs.* 1/T, as shown in Fig. 7, the activation energy can be deduced and it was found to equal 3.86 kJ/mole.

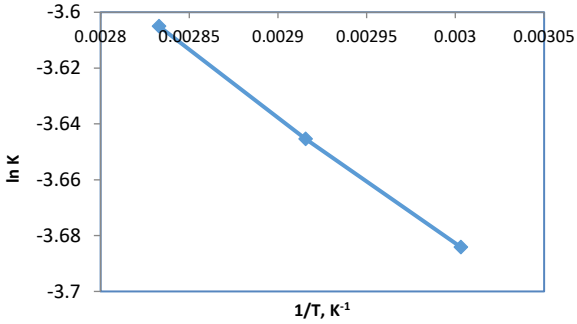

Fig. 7 Plot of ln K Vs. 1/T at 40% NaOH

4. Conclusion

2^3 Full factorial design was used to assess the best conditions for chitosan production from shrimp shells by reaction with sodium hydroxide through deacetylation reaction. The investigated parameters are sodium hydroxide concentration, reaction time, and temperature. A first order model was first elaborated, and a regression equation obtained that showed a strong determination coefficient (0.946). The regression equation shows no maximum as all terms are positive and it also shows that there is no interaction between the three studied parameters. It was found that sodium hydroxide concentration had the highest impact on the deacetylation reaction. It is recommended to consider the optimum conditions at 80 °C 50% NaOH and a time range from 3 to 4 h. The deacetylation reaction was found to be endothermic first order reaction of reaction rate constant equals 0.0268 h^{-1} and activation energy of 3.862 kJ/mole.

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