Optimization of the Green Synthesis of Tin Oxide Nanoparticles by Response Surface Methodology (RSM) using Box-Behnken Design

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Abstract

In this paper, tin oxide nanoparticles (Nps) was synthesize via green route using $SnCl_2.2H_2O$ and *Euphorbia trigona* (African cactus) plant extract as precursors. Process parameters such as solution pH, precursor concentration and synthesis temperature were optimized to produce Nps with smaller size. The level of sensitivity of the synthesis parameters towards response and the optimization was carried out by applying the Box-Behnken Design from Response Surface Methodology (RSM). The Box-Behnken Design was selected as a statistical prediction method with the aim of reducing the number of experimental runs, which would invariably save time and chemicals, thereby reducing the overall cost of production. The size of the nanoparticles was selected as the response factor for the green synthesis. The optimum predicted conditions obtained for SnO_2 were at a solution pH of 10, precursor concentration of 0.40 M and synthesis temperature of 57.5°C. The particle size from the optimized experimental conditions was found to be 6.71 nm, which was also found to be in good agreement with predicted value of 6.73 nm from the developed models. These result was justified by the relatively high correlation coefficients of SnO_2 Nps (R^2= 99.96, R_{adj} =99.87, R^2_{pred} =99.28) obtained from the statistical prediction after the Analysis of Variance (ANOVA).

Keywords: Tin Oxide, Optimization, Response surface Methodology, Box-Behnken, Green synthesis.

1.0 INTRODUCTION

Nanoparticles have attracted great interest due to their intriguing properties, which are different from those of their corresponding bulk state. Enormous efforts are being taken towards the development of nanometer sized materials in studies related to one hand to their fundamental mechanism such as the size effect and the quantum effect and on the other hand towards application of these materials (Merlin et al., 2018).).Green synthesis involves the use of plant phytochemicals which have antioxidant property is mainly responsible for the preparation of metal and metal oxide nanoparticle. Besides, many biological components have abilities to act as templates in the synthesis and help to produce a self assembled nanoscale material (Khan et al., 2013; Courchesne et al., 2014). Tin oxide (SnO_2) has been studied intensely because of its potential applicability to lithium-ion batteries (Chen and Lou, 2013), transparent conducting electrodes in ionic devices (Chopra, 1983), anti-reflective coatings (Minami, 2000) solid-state gas sensors, solar cells (Shang et al., 2012), catalytic support materials (Sharghi et al., 2013), energy storage (Kalubarme et al., 2015), medicine (Sudhaparimala, 2014).

Studies by Akhir et al. (2016) have developed SnO_2 nanoparticles of different sizes by adjusting parameters such as, precursor concentration, treatment temperature and reaction time, while Ba-Abbad et (2015) optimized process parameters such as, molar ratio of precursors, solution pH, and calcination temperature. In addition, it has also been reported that the type of solvent used has dominant effect on the surface morphology and properties of nanoparticles. Organic solvents, such as ethanol, have been reported to be the best solvents for reducing the size of nanoparticles due to their ability to control the nucleation process and its crystal orientation (Phindile, et al., 2012). In order to optimize these important process parameters with the aim of minimizing the nanoparticle sizes, methods such as the Response Surface Methodology (RSM) have been applied recently (Ba-Abbad, 2013). The optimization process by RSM includes three main steps: (a) selection and implementation of the appropriate experimental design, (b) estimation of all the coefficients of the model from the developed mathematical model using analysis of variance (ANOVA), (c) validation of the final model by prediction and

experimental runs of the process response (Senthilkumar et al., 2013). In this study, the main objective is to control the size of SnO_2 NPs synthesized by green route under different process conditions. The Response Surface Methodology (RSM) based on Box–Behnken designs of experiment was selected in order to determine and optimize the effects of the process conditions on the response, which is the SnO_2 particle size. The Box–Behnken design is a three-level factorial design for three factors with selected points from a system arrangement. The advantage of this design is that it can reduce the number of runs and can be used for a large number of factors in one process (Jafarzadeh et al., 2011).

2.0 Experimental

2.1 Materials and methods

The following chemicals $SnCl_2 2H_2O$ (98.8%) and (NaOH) (99.99 % purity) were obtained from Merck, India and used as supplied without any further purification.

2.2 Synthesis of SnO_2 nanoparticles

The green synthesis of SnO_2 was carried out as follow: 20 cm^3 of 0.40 M $SnCl_2 2H_2O$ solution was added to 50 cm^3 of plant extract, and the resulting mixture was heated at 80°C for 2 h after adjustment of the pH to 10 using 1 M solution of NaOH. The greenish yellow coloured solution changed into pale yellow, which indicated the formation of tin oxide nanoparticles. The pale yellow precipitates formed were centrifuged to remove the residual particles and then dried in an oven at 80°C for 6 h and further calcined at 500°C for 3 h. The obtained samples were pulverized with an agate mortar and stored in sterile sample bottle for further use.

2.3 Characterization of SnO_2 Nanoparticles

The surface morphology and elemental composition nanoparticles were confirmed by High Resolution Scanning Electron Microscopy (HRSEM, FD 1250), which was coupled with Energy Dispersive Spectroscopy (EDS). X-Ray Diffraction (XRD, Bruker D8 Advance AXS) with condition of the X-ray diffraction run designated as Cu K alpha radiation (1.5406 Å) in the 2θ scan range of 20-80° for all experiment was used to determine the crystalline phases present in the nanoparticles.

2.3 Orthogonal array Box–Behnken design

The Box–Behnken design is a second-order technique based on three-level factorial design for three factors and more with selected points from a system arrangement (Jafarzadeh et al., 2013).

The number of experimental runs required (N) is calculated by N=2k (k-1) + C, where the number of factors is k and the centre point is C. The main advantage of this design is that it can reduce the number of runs and can be used for a large number of factors in one process. To improve the performance of the Box–Behnken design, the three levels of the factors should be adjusted as −1 (lower), 0 (medial) and +1 (higher) (Alaoui et al., 2015). The Box-Behnken design for the three levels synthesis of SnO2 Nps are presented in Table 1.

Table 1: Factors with their levels for SnO_2 NP synthesis

Factors	Levels		
	-1	0	1
Solution pH (X_1)	10	11	12
Precursor concentration (X_2)	0.350	0.375	0.400
Synthesis temperature (X_3)	25.0	57.5	90.0

The advantages of Box-Behnken design compared to other surface design is that it is more efficient where the efficiency of one experimental design is defined as the number of coefficients in the estimated model divided by the number of experiments (Alaoui et al., 2015).). Minitab ® software (based on the Box–Behnken design was applied to optimize SnO_2 NPs synthesis following the quadratic polynomial in Equation (1).

$$Y = \beta_0 + \sum_{i=j}^{k} \beta_i X_i + \sum_{i=j}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

Where Y is the predicted response (target of study), β_i are the coefficients of the linear terms, β_{ii} are coefficients of the quadratic terms, β_{ij} are coefficients of the interaction factors, X_i and X_j indicated the independent variables and ε is the random error. The mathematical relationship between the three factors X_1, X_2 and X_3 with their coefficients represented by a second order calculation in Equation (2):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (2)$$

In this study, the following parameters that affect the synthesis of SnO_2 NP by green synthetic route were chosen as; (i) the pH of the solution, (ii) tin precursor concentrations and (iii) the synthesis temperatures.

Table 2: Experimental runs of Box–Behnken design with comparison between predicted and experimental size of SnO_2 NPs

Std Order	Run Order	X_1	X_2 (moldm^{-3})	X_3 (°C)	Y_0 (nm)	Y_1 (nm)
13	1	11	0.3750	57.50	9.85	9.86
6	2	12	0.3500	57.50	14.14	14.14
7	3	10	0.4000	57.50	6.71	6.73
11	4	11	0.4000	25.00	9.16	9.24
1	5	10	0.3750	25.00	7.35	7.28
4	6	12	0.3750	90.00	11.51	11.60
3	7	10	0.3750	90.00	6.81	6.80
12	8	11	0.4000	90.00	7.89	7.90
8	9	12	0.4000	57.50	13.56	13.49
14	10	11	0.3750	57.50	9.85	9.86
15	11	11	0.3750	57.50	9.85	9.86
2	12	12	0.3750	25.00	13.42	13.45
10	13	11	0.3500	90.00	10.05	10.00
9	14	11	0.3500	25.00	10.98	10.99
5	15	10	0.3500	57.50	9.84	9.93

Y_0 = Experimental response (particle size)

Y_1= Predicted responses (particle size)

3. Results and discussion

3.1 Model fitting and ANOVA analysis

The main factors influencing the synthesis of d SnO_2 NPs was investigated to produce minimum particle size. Therefore, a set of experimental runs were determined to identify the effect of each of these factors as well as the range for SnO_2 NPs sizes. All experiments were conducted in triplicate to verify the optimum conditions for the synthesis and also to validate the adequacy of the final predictions. Evaluation of the fitted models is very important to ensure adequate predictions of the results compared to the experiments. The prediction models SnO_2 NPs optimization based on Box Behnken design is presented in Equations (3).

$$Y_0 = 285.5 - 22.33X_1 + 0.2255X_3 - 888.9X_2 + 0.7325X_1^2 - 0.000767X_3^2 + 768.0X_2^2 - 0.01054X_1X_3 + 25.50X_1X_2 - 0.1046X_2X_3 \quad (3)$$

Where, Y_0 is the response (particle size in nm) for SnO_2. X_1, X_2, and X_3 are the process factors of Solution pH, precursor concentration and synthesis temperature respectively. As shown in Table 2, a good agreement exists between the predicted results and those obtained from experiments. The ANOVA result for SnO_2 NPs synthesis are presented in Table 3. The second order regression model for SnO_2 NPs were found with a significantly high confidence level (95%). For SnO_2 the R^2 of 0.9996 also indicates high validity for the predicted Np sizes. Furthermore the (R^2(adj) =0.9987, R^2(pred) = 0.9928) values that the final prediction is in good agreement with the experimental results. The F-value of the synthesis process was found to be 1237.84, also implied that the prediction was significantly better.

Table 3: ANOVA results for quadratic model of SnO_2 NP using Box Behnken design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	77.9284	8.6587	1237.84	0.0000*
Linear	3	70.1556	23.3852	3343.13	0.0000*
X_1	1	60.0608	60.0608	8586.25	0.0001*
X_3	1	2.7028	2.7028	386.39	0.0002*
X_2	1	7.392	7.392	1056.76	0.0004*
2-Way Interaction	3	2.1238	0.7079	101.2	0.0001*
X_1X_3	1	0.4692	0.4692	67.08	0.0001*
X_1X_2	1	1.6256	1.6256	232.4	0.0001*

X_2X_3	1	0.0289	0.0289	4.13	0.098**
Error	5	0.035	0.007	---------	---------
Lack-of-Fit	3	0.035	0.0117	---------	---------
Pure Error	2	0	0	---------	---------
Total	14	77.9634	---------	---------	---------

*Significant at < 0.05% level; ** Not significant, R^2 = 0.9996, R^2(adj) =0.9987, R^2(pred) = 0.9928, S=0.0836361.

3.2 Adequacy of the regression model

In order to optimize relatively smaller size NPs by avoiding poor and undesired results, a fit of the (synthesis) experimental data was performed and presented in Fig 1. The Fig shows all the diagnostic plots of SnO_2 NPs optimization to evaluate the adequacy of the regression model of prediction. The normality of results was checked by plotting the normal probability versus standardized residuals (estimated from standard deviation) as shown in Figs 1(a). The results showed that all experiments were near the continuous line that was attributed to the fact that no obvious problems with the normality of the design were observed. The effect of standardized residuals and the predicted particle size was a random scattering of all points rather than a funnel-shaped pattern, which indicated that the response had an original observation of variance and that there was no problem with the predicted particle size. Generally, from Figs 1 (b) the values of the standardized residuals have to be always within the interval of -3.5 to +3.5, and the observed particle size value should not be considered for any value beyond these values (Rauf et al., 2008). In this study, SnO_2 NPs optimization had a standardized residual value that was lower than ±2 as presented in Figs 3 (b), which gives a good fitting of the prediction. Furthermore, the outlier of the observation runs shows a good distribution as presented in Fig.1(c), with no run out of the considered range. To assess the validity of the prediction, the predicted values of SnO_2 NPs sizes were compared to experimental ones and are given in Figs 1 (d). These results show that the predicted and experimental points are in a good agreement as illustrated by all points arranged very closely to the diagonal line.

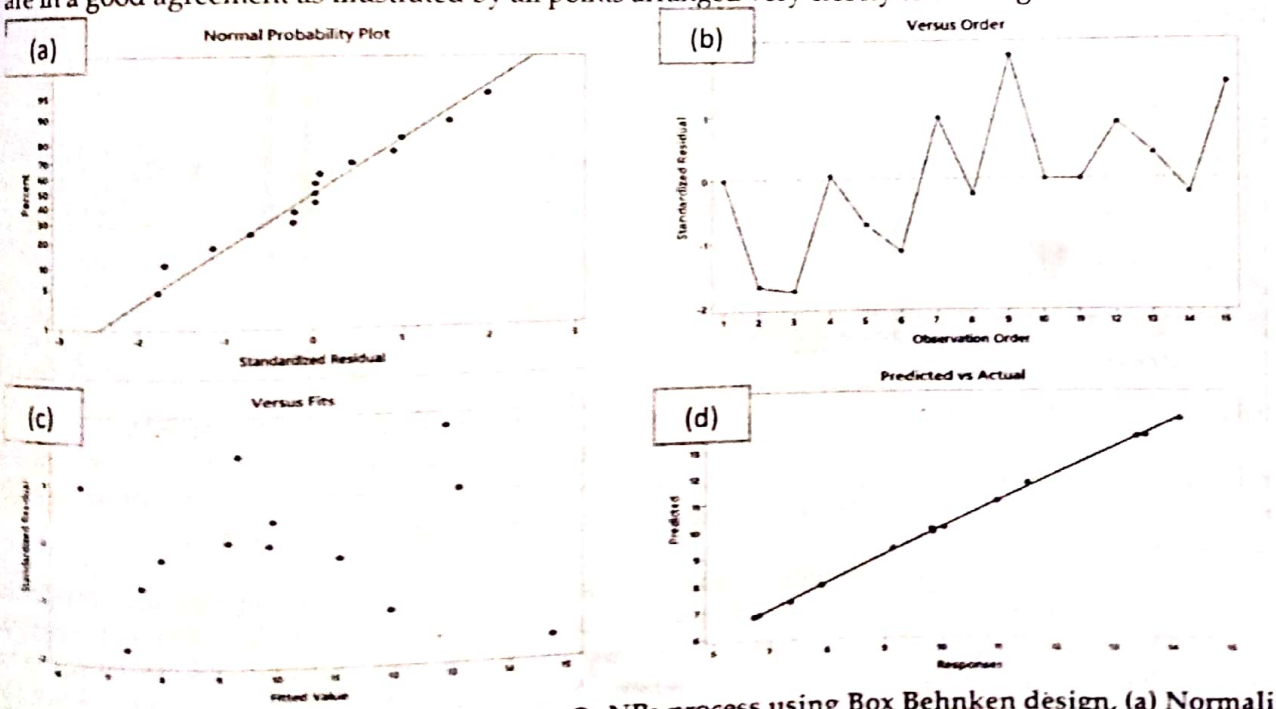

Fig 1: All diagnostic plots of optimization SnO_2 NPs process using Box Behnken design, (a) Normality, (b) Standardized residuals, (c) Outlier T, (d) Actual and predicted size of SnO_2 NPs

3.3 Effect of Synthesis Factors as Surface and contour Plots

The effect of each factor on the synthesis of SnO_2 NP was investigated in a 3-D response surfaces and contour (2-D) graphs created using the second order polynomial model. Fig 2 shows the effect of the different interaction between all the factors by varying two factors within the experimental ranges. These effects were explained individually using statistical values with more evidences to how the effects occurred within the varying of the factors ranges.

In Fig 3(a) the peaks of 2θ values of 26.6°, 33.89° and 54.76° are associated to (110), (101), and (220) respectively are in accordance to the JCPDS card no. 41-1445. The crystal planes showed that the nanoparticles are polycrystalline.

The average crystallite sizes are calculated using the Scherrer equation. The average crystallite sizes were found to be 6.71 at pH 10. The Morphology of the SnO_2 synthesized via green synthesis procedure strongly depends on the amount of H^+ or

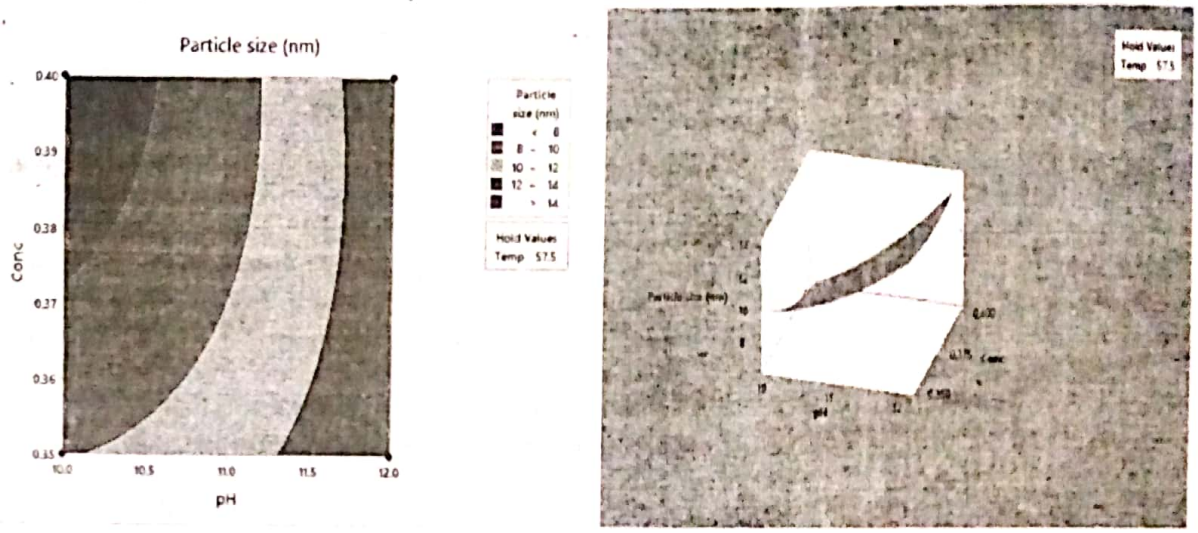

Fig. 2: Effect of interaction between solution pH and precursor concentration on the SnO_2 NP size as 3D response surface and 2D contour plot.

3.4 Characterization of the snO_2 Nps

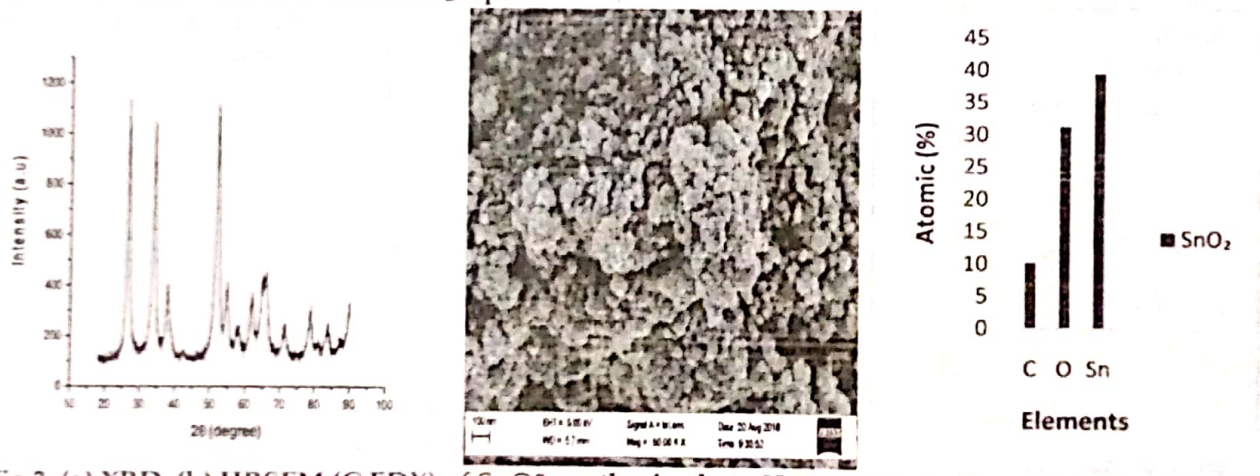

Fig 3: (a) XRD, (b) HRSEM (C EDX) of SnO2 synthesized at pH 10, concentration of 0.4 M and 57.5°C

OH^- ions in the solution. Tin oxide synthesized when the solution pH is 10 and calcined at 500 °C, is presented in Fig 3(b) and shows agglomerated spherical shaped structures. While the EDX Fig 3 (c) showed the presence of tin, oxygen and carbon from the plant origin. The XRD pattern of SnO_2 at pH 10 are shown in Fig 3 (c).

4.0 Conclusion

The synthesis of SnO_2 Nps using green synthesis was successfully achieved by varying synthesis conditions. Statistical design of experiment based on Box-Behnken design with three variables (solution pH, precursor concentration, and synthesis temperature) was used to study the effect of each variable with crystal size of as-synthesized SnO_2 Nps. It was noticed that the solution pH had most significant effect on crystal size followed by precursor concentration and synthesis temperature. Based on Box-Behnken design, the smallest crystal size (6.71 nm) was obtained when the solution pH was 10, precursor concentration was 0.40 M and synthesis temperature was 57.5 C. Response surface methodology (RSM) analysis of the crystallite size effect with respect to the above variables showed that it could identify important factors that governed reaction mechanism in forming Nps.

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