Nigerian Journal Of Materials Science and Engineering

(NJMSE)

Volume 10 Issue 1 ISSN 214-453-2 May 2020

Materials Science & Technology Society of Nigeria (MSN)

Nigerian Journal of Materials Science and Engineering

Volume 10 Issue 1 May 2020

ISSN 214-453-2

An International Journal of the Materials Science and Technology Society of Nigeria

Nigerian Journal of

Materials Science and Engineering (NJMSE)

Materials Science & Technology Society of Nigeria (MSN)

Volume 10 Issue 1, May 2020
ISSN 214-453-2

Published by

Materials Science and Technology Society of Nigeria (MSN)
National Headquarters
Engineering Materials Development Institute (EMDI)
Km. 4 Ondo Road,
P. M. B. 611, Akure. Nigeria
Tel.: +234-803-471-8487; +234-803-703-3052; +234-806-220-7420

http://njmse.msn.ng
NJMSE@msn.ng; njmse.msn@gmail.com; editorinchief@msn.ng; njmsemanagingeditor@msn.ng;
bbabatop@oauife.edu.ng;giwafat2002@yahoo.com

(NJMSE - An International Journal of the Materials Science and Technology Society of Nigeria)

NJMSE Editorial Board

Editorial Comment

It is a great pressure for the editorial board of the Nigerian Journal of Materials Science and Engineering (NJMSE) to present Volume 10 Number 1 of the journal for 2020 for the world research and development community.

The Materials Science and Technology Society of Nigeria (MSN), as a professional learned body, has made the publication of this research journal to be of very good quality and high standard comparable to any in her class. Our major thrust is to disseminate materials science and engineering and allied research activities from Nigeria, Africa and the world over. We are slowly and gradually impacting on the research community work with this specialised journal from a reputable learned and professional body in Nigeria. We are presently not insisting on number but we very much believe, with the thoroughness of our approach to the review and assessment process, we are convinced that with our resolve to publish quarterly, the board is convinced that more researcher would take advantage of this.

As a journal whose policy is to maintain the standard best practices and in addition to help young researchers to advance in the art and science of scientific findings dissemination, had faced tremendous challenges which were expected. It is heart-warming that we can look back and be glad to see the society publishing the 10th volume. These volumes and the previous ones would be available for FREE downloading on our society website (www.msn.ng) through a link prior to the specialised journal website to be available soon. Arrangements are in advanced stages for the hosting of this journal by reputable international online submission system are being worked on.

Volume 10 (2020) Number 1 consists of eight (8) high standard articles covering different specialised areas of materials research. It is our hope that this humble effort, presently by voluntary efforts of senior members of the Society, at disseminating research findings as put together in this volume which have contributed to the body of knowledge, would have enriched the information base and complemented Materials Research efforts from around the world.

We appreciate all our reviewers and associate editors involved for their prompt action on the manuscripts and cooperation as we look forward to submission of manuscripts which can be forwarded as detailed below.

Babaniyi Babatope. (PhD,MBA,FMSN,FIMMM(UK))
Editor-in-Chief.
Department of Physics and Engineering Physics,
Advanced Nanostructured Materials and Devices Research Group
Obafemi Awolowo University, Ile-Ife. Nigeria.
bbabatop@oauife.edu.ng
editorinchief@msn.ng; njmse.editor.in.chief@gmail.com.

Manuscripts can also be submitted and copied to:

Managing Editors, NJMSE.
njmsemanagingeditor@msn.ng; njmse.msn@gmail.com; njmse@msn.ng.

Editor-in-Chief
editorinchief@msn.ng;njmse.editor.in.chief@gmail.com

Website:
http://njmse.msn.ng/

GUIDE TO AUTHORS

AIM: *T*o improve the international exchange of scientific research in materials science and engineering.

INTRODUCTION

The Nigerian Journal of Materials Science and Engineering (NJMSE) publishes reviews, full-length papers, and short communications recording original research results on, or techniques for studying the relationship between structure, properties, and uses of materials. The subjects are seen from international and interdisciplinary perspectives covering areas including metals, ceramics, glasses, polymers, composite materials, fibers, electronic materials, alternative energy materials, nanostructured materials, nanocomposites, biological, biomedical materials, etc. The NJMSE is now firmly established as the leading source of primary communication for scientists investigating the structure and properties of all engineering materials in Nigeria, Africa and the Rest of the World.

UNIQUENESS OF THE JOURNAL

NJMSE is introduced to publish research findings on current topical issues of interest to both public and private sectors. The scope of the Journal focuses on experimental, empirical and theoretical research in Materials Science and Engineering. Findings from multidisciplinary research covering diverse areas of interest with potential impact on the public and private sectors of both the national and international communities will be priorities of the journal. Our major focus is the use of Materials Science and Engineering principles to solve basic problems peculiar to African and the developing world while contributing to knowledge on the global scale.

GUIDE FOR AUTHORS

NJMSE welcomes research papers covering original work that has good potential for practical application. Submission of a manuscript will be held to imply that the work being reported is original and that the result has not been published previously nor been under considerations for publication elsewhere.

MANUSCRIPT PREPARATION

The format of the typescript should be as follows:

The official language of the journal is English. When writing <u>do not mix languages</u>, use US English completely or use UK English completely. It is expected that before submission, the manuscript will have been thoroughly reviewed and written in simple clear expression. Manuscript should be typewritten with <u>double-spacing and 2.54 cm or 1 inch margins on all sides</u>. Manuscripts should be submitted in electronic form and e-mailed directly to the addresses below in MS-Word format, double spacing with graphics at the end. Manuscripts should be arranged in the following order: title page, abstract, introduction, materials and methods, results and discussion, conclusions, acknowledgements, references. The manuscripts should follow the format listed below.

Title: The title page should contain the title [concise but clear expression, written in bold, upper case], followed by the authors [surname first, block letters throughout], and followed by their institutional affiliations and the e-mail address of the corresponding author. In case of many authors, please use numbers to differential their affiliation.

Abstract: An abstract of not more than 350 words should be supplied immediately before the beginning of the paper (Graphical abstracts are also acceptable).

Introduction: This should contain a brief review of literature, clearly stated objectives and justification for the study.

Materials and Methods: This should contain materials preparation procedure and major measurement patterns. Sufficient information should be provided to perform repetition of the experimental work.

Results and Discussion: The result section should contain appropriate tables, figures/illustrations**.** These should be pertinent to the work and should clearly indicate the degree of reliability of results. Tables should be numbered consecutively, with a short descriptive title in upper case (block letters) on top of the table. They should contain no vertical lines and no lines to separate the rows except the heading and the end of the table. Figures, micrographs, or illustrations must be clearly captioned, the captions at the bottom of each figure. Figures may not be used to repeat the information already presented in tables or text or vice versa. Micrographs and illustrations are considered as figures and must be labeled as such.

Conclusions: These should summarize any important conclusions emerging from the work.

Acknowledgements: These should be presented at the end of text and before the references. Technical assistance and advice may be acknowledged. Acknowledgments of financial support can also be stated in this section.

References:

Citing: Reference in the text should be made by the author's last name and year of publication, e.g. (Abel, 2007); (Abel and Babcock, 2007); (Bowen *et al*., 2007). Two papers by the same author in the same year should be distinguished by a suffix, (a, b, etc) e.g. (Madonna, 2006a); (Madonna, 2006b).

Listing: This should be in alphabetical order and should follow this format: Name(s) and initial(s) of author(s), (year of publication), exact title of paper (in quote), the title of periodical, Vol. (number)**:** initial and final page numbers. Please note that only name cited in the text can be used.

Serial: Briant C. L. and Banerji S. K. (1981). Tempered Martensite Embrittlement and Intergranular Fracture in an Ultrahigh Strength Sulfur Doped Steel, *Metall. Trans. A,* 12A:309-319. (Please pay attention to punctuations).

Book: Samuels, L.E. (1982). *Metallographic Polishing by Mechanical Methods,* 3ed., American Society for Metals, Metals, Park, Ohio.

Proceeding: Olorunnisola A. O. (2006). The potentials of bamboo as novel building and furniture production materials in Nigeria, pp.180-185. In *Proc. Nigerian Materials Congress (NIMACON 2006),* (B. Babatope and W.O. Siyanbola, Eds.), organized by Materials Society of Nigeria, 15-18 November 2006, Abuja, Nigeria.

Heading and sub-heading: All headings and sub-headings should be numbered and started from the left hand margin. All headings should be in upper case while sub-headings should be in lower case except the first letter.

Equations: Equations should be distinctly typed using Microsoft equation. Avoid powers of "e" and use "exp". Equations should be numbered consecutively by Arabic numerals in parenthesis at the right margin. In the text, such equation should be cited as Equation (1) etc.

Units and symbols: Symbols, units and nomenclature should conform to the recommendations of the International Union of Pure Applied Chemistry (IUPAC). SI units should be used for physical quantities.

Peer-Review: All submitted manuscripts are subjected to a peer- review process and galley proofs will be sent to the first or corresponding author where necessary.

SUBMISSION OF MANUSCRIPTS

A Processing Fee of N10,000.00 only is payable per article. All submitted articles MUST be accompanied with scanned Bank (detail below) Tellers or On-line transfer receipt as evidence of payment. Send your article(s) and Bank Teller to: njmse@msn.ng; NJMSE.msn@gmail.com. All submission of manuscripts must be sent on-line to fast-track processing and simplify the refereeing process.

PAGE CHARGE

Corresponding Authors of accepted articles will be required to pay a sum of N10,000.00 only as processing fee (at the point of acknowledging receipt of manuscript) and N10,000.00 (non-members and non-financial members of MSN), N5,000.00 (financial members of MSN) after acceptance (or $100.00 USD for processing and acceptance for other countries). They will receive free ecopy of the NJMSE volume in .pdf version. The ecopy is available online at http://njmse.msn.ng and can be downloaded free. However, printed copy(ies) may be requested for extra payment.

COPY RIGHT

Submission of an article for publication implies the transfer of the copyright of the manuscript from the author(s) to the publisher upon acceptance and that the manuscript has not been previously published elsewhere. This is the responsibility of the authors. Accepted papers become the permanent property of the publisher and may not be reproduced by any means without the written consent of the Editor-in-Chief.

Account Details: GTB PLC A/C No. 0171794514. Materials Science and Technology Society of Nigeria.

All Correspondence to:

Prof. A. Giwa
NJMSE Managing Editor
Department of Polymer and Textile Engineering
Ahmadu Bello University
Zaria. Nigeria. +2348037033052; +2348025672474
giwafat2002@yahoo.com.

Engr. Adetunji Ogunkoya
NJMSE Desk /Processing Officer,
Engineering Materials Development Institute (EMDI)
Ondo Road, PMB 611,
Akure Nigeria. +2348062207420;+2347081019516

http://njmse.msn.ng/
Emails: njmse@msn.ng; njmse.msn@gmail.com; njmsemanagingeditor@msn.ng; editorinchief@msn.ng; njmse.editor.in.Chief@gmail.com; .

Page No

TABLE OF CONTENT

Kareem, A.G. et.al.: Nigerian Journal of Materials Science and Engineering.. Vol. 10(1):10-17 (2020)

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

Kareem Aduagba Ganiyu; [1]**Abdulrahman** Asipita Salawu;
[2]**Abdulkareem** Ambali Saka and [3]**Tijani** Jimoh Oladejo

Department of Mechanical Engineering, Federal University of Technology, PMB 65, Gidan Kwano Campus, Minna, Niger State, Nigeria.
[1]Department of Material and Metallurgical Engineering, Federal University of Technology, PMB 65, Gidan Kwano Campus, Minna, Niger State, Nigeria.
[2]Department of Chemical Engineering, Federal University of Technology, PMB 65, Gidan Kwano Campus, Minna, Niger State, Nigeria.
[3]Department of Chemistry, Federal University of Technology, PMB 65, Gidan Kwano Campus, Minna, Niger State, Nigeria.

E-mail: agaduagba@gmail.com

Abstract

Tin oxide nanoparticles has been synthesized via green route using $SnCl_2.2H_2O$ and *Euphorbia trigona* (African cactus) plant extract as precursors. In this green route process parameters such as, solution pH, precursor concentration and synthesis temperature were optimized to produce nanoparticles with smaller size. The degree of sensitivity of the process parameters vis-a-viz towards optimization were carried out by applying the Box-Behnken Design from Response Surface Methodology (RSM). The Box-Behnken Design was designated as a statistical prediction technique with the goal of decreasing the number of possible experimental outcomes, which would invariably reduced time and quantity of reagents, by this means plummeting the general cost of the production process. The particle size of the nanoparticles was chosen as the response factor for the green synthesis. The optimal predicted conditions obtained tetragonal cassiterite phase of SnO_2 were at a solution pH of 10, precursor concentration of 0.40 M and synthesis temperature of 57.5°C. From the optimized experimental conditions, the particle size was found to be 6.71 nm, which was also found to be in accordance with predicted value of 6.73 nm from the developed model. These results were substantiated by the comparatively high correlation coefficients of SnO_2 NPs (R^2= 99.96, R^2_{adj}= 99.87, R^2_{pred} =99.28) obtained from the statistical prediction after the Analysis of Variance (ANOVA).

Keywords: Tin oxide, Response Surface Methodology, Box-Behnken Design, Green synthesis.

INTRODUCTION

Nanoparticles have pulled in extraordinary enthusiasm because of their captivating properties, which are not the same as those of their comparing bulk state. Immense endeavors are being taken towards the advancement of nanometer measured materials in studies associated on one hand to their fundamental mechanism such as size and quantum effects (Merlin *et al*., 2018).

Several physical and chemical methods such as solvothermal, hydrothermal, sol-gel, thermal evaporation, microwave assisted reduction, spray pyrolysis, photoreduction have been utilised to produce Tin (IV) oxides nanoparticles. However, these methods have complex procedures, required the use of toxic and expensive reagents and also generate toxic by-products amongst others. On the other hand, green synthesis of metal and metal oxide nanoparticle is considered simple and utilise either plant or microbes to reduce complex metal salts to their zero valence states. The plants phytochemicals act as reducing, capping and stabilizing agents. The plants metabolites include, tannins, saponins, flavonoids, phenols, anthraquinones, alkaloids to mention but a few.

More so, many biological components have abilities to act as templates in the synthesis (reducing and capping agents) and help to produce self-assembled nanoscale materials (Courchesne *et al*., 2014).

An eco-friendly and green synthesis of metallic nanoparticles have been reported using plant extracts such as using *Pisonia alba* leaf extract as well as gelatin and maltose, a non-toxic disaccharide in the synthesis of MgO and Ag nanoparticles respectively (Oluwafemi *et al*., 2013; Sharmila *et al*., 2019). Consequently, SnO_2 have been synthesized via a green protocol using *Averrhoa bilimbi* fruit extract in recent times (Sunny, and Venkat, 2019).

Tin oxide (SnO_2) has been studied extensively because of its promising utilization in 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) and many others.

Studies by Akhir *et al*. (2016) produced SnO_2 nanoparticles of different sizes by adjusting parameters such as, precursor concentration, treatment temperature and reaction time, while Ba-Abbad *et al*. (2016) optimized process parameters such as, solution pH, molar ratio of precursors, and calcination temperature during the synthesis of other metallic oxide nanoparticles. Additionally, it has been accounted for that the kind of solvent utilized has predominant impact on the surface morphology and properties of nanoparticles. Organic solvents, for example, ethanol, have been accounted for to be the best solvents for lowering the size of nanoparticles because of their capacity to control the nucleation procedure and its crystal direction (Phindile, *et al*., 2012). To optimize these essential process parameters with the goal of minimizing the nanoparticle sizes, techniques such as the Response Surface Methodology (RSM) have been utilized (Ba-Abbad, 2013).

The optimization system by means of RSM consists of three major steps: (a) determination and implementation of the suitable experimental design, (b) estimation of all the coefficients of the model from the developed mathematical model by the use of analysis of variance (ANOVA), (c) validation of the final model via prediction and experimental outcomes of the process response (Senthilkumar *et al*., 2013).

The major objective of this study is to control the size of SnO_2 nanoparticles synthesized by green route under different synthesis parameters such as, solution pH, precursor concentration, and synthesis temperature. The Response Surface Methodology (RSM) centered 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. One of the benefit of this design is that it can reduce the total runs and can be used for a large number of factors in one process (Jafarzadeh *et al*., 2011).

EXPERIMENTAL

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.

Preparation of the Aqueous Extract of African Cactus

A known weighed (5 g) of the leaves was added to 100 cm^3 of distilled water in a 250 cm^3 conical flask. The resulting mixture was stirred and heated at 80°C for 90 min and then filtered using No 10 Whattman filter paper. The filtered extract was stored at 4°C in a refrigerator until further use.

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 due to a bio-reduction by the aqueous plant extract. 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.

Characterization of SnO_2 Nanoparticles

The surface morphology and elemental composition of the 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 Kα 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.

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 array (Jafarzadeh *et al*., 2011).

The number of experimental outcome 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 benefit of this design is that it can decrease the number of runs and can be used for plenty number of factors in one process. To increase the functioning efficiency 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 SnO_2 nanoparticles is as presented in Table 1.

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 nanoparticles 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 is presented in Equation (2) as:

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

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

Table 1: Factors with their Levels for SnO_2 Nanoparticles 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

RESULTS AND DISCUSSION

Model Fitting and ANOVA Analysis

Key factors influencing the synthesis of SnO_2 nanoparticles was investigated to produce minimum particle size. Therefore, a set of experimental outcomes were determined to identify the effect of each of these factors as well as the range for SnO_2 nanoparticles sizes. All experiments were conducted in triplicates 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 nanoparticles optimization based on Box Behnken design is presented in Equation (3).

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

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 nanoparticles synthesis are presented in Table 3. The second order regression model for SnO_2 nanoparticles 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 nanoparticles sizes. Furthermore the (R^2(adj) = 0.9987, R^2(pred) = 0.9928) values points out that the final prediction is in conformity with the experimental results. The F-value of the synthesis process was found to be 1237.84, and also implied that the prediction was significantly accurate.

Adequacy of the Regression Model

In order to optimize relatively smaller size nanoparticles by avoiding unwanted and poor results, a fit of the synthesis data was executed and presented in Figure 1. The Figure shows all the analytical plots of SnO_2 nanoparticles optimization to estimate the acceptability of the regression model of prediction. The normality of results was verified by plotting the normal probability versus standardized residuals (estimated from standard deviation) as shown in Figure 1(a). The results showed that all experiments were near the continuous line that was attributable to the fact that no anomaly with the experimental runs were observed during the design. The effect of standardized residuals and the predicted particle size was a random scattering of all factors 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 estimated particle size. Generally, from Figure 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 accepted beyond these values (Rauf *et al*., 2008).

In this study, SnO_2 nanoparticles optimization had a standardized residual value that was within the range of ±2 as presented in Figure 3(b), which gives an acceptable fitting of the prediction. Furthermore, the outlier plot of the observation runs shows a good distribution as represented in Figure 1(c), with no run out of the studied range. To measure the cogency of the prediction, the predicted values of SnO_2 nanoparticles sizes were contrasted to experimental ones and are represented in Figure 1(d). These results show that the

Table 2: Experimental runs of Box–Behnken Design in Comparison Between Predicted and Experimental Size of SnO_2 Nanoparticles

Std Order	Run Order	X_1	X_2 (mol.dm^{-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)

Table 3: ANOVA Results for Quadratic Model of SnO_2 Nanoparticles 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	---------	---------	---------

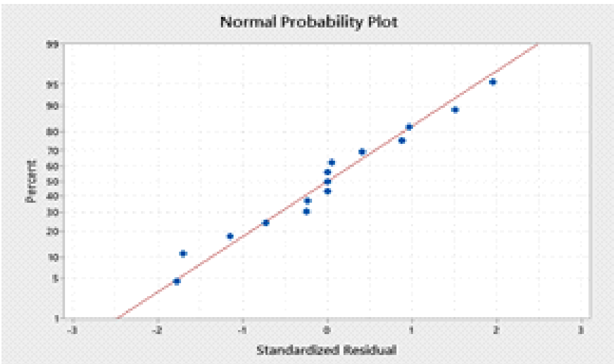
*Significant at < 0.05% level; ** Not significant, R^2 = 0.9996, R^2(adj) =0.9987, R^2(pred) = 0.9928, S=0.0836361.

experimental and predicted values are in a good agreement as illustrated by all points distributed very closely to the diagonal line.

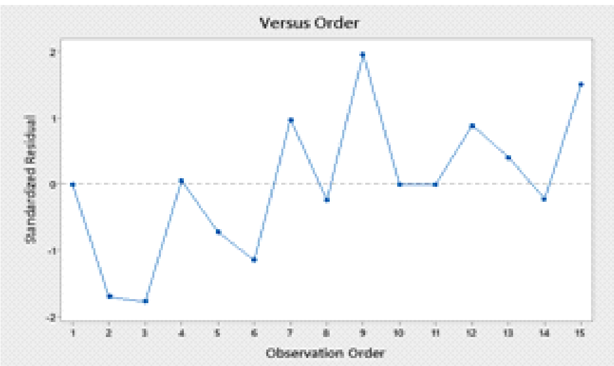
Effect of Synthesis Factors as Surface and Contour Plots

The effect of each factor on the synthesis of SnO_2 NPs was examined in (3-D) response surfaces and contour (2-D) graphs created using the second order polynomial model. Figure 2, shows the effect of the effect of varying solution pH and precursor concentration within the experimental ranges. These effects were described independently using statistical values with more indications to how the effects occurred during the variation of each process parameter.

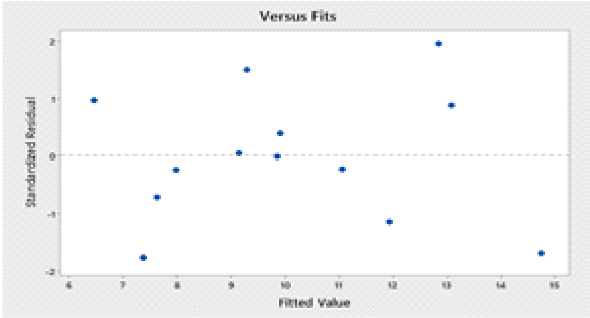
For the pH range (10-12), after the addition of ammonium hydroxide (NaOH), the pH of the solution increases, however, the smallest crystallite sizes were obtained when the pH value was lowest (10). In solution, the ratio of OH^- ions and Sn^{+2} ions are stoichiometric, therefore, as the pH begins to increase from 10 to 12, the size of the nanoparticles also increase rapidly. Plausibly, the elevated pH value created a high super saturation level due to the large concentration of hydroxyl ions in solution, resulting in an extremely fast nucleation process generating tiny nuclei (Yan *et al.*, 2009). The tiny nuclei that form will dissolve and re-precipitate on the growing secondary particles through Ostwald ripening as given in the Equations (4-8).



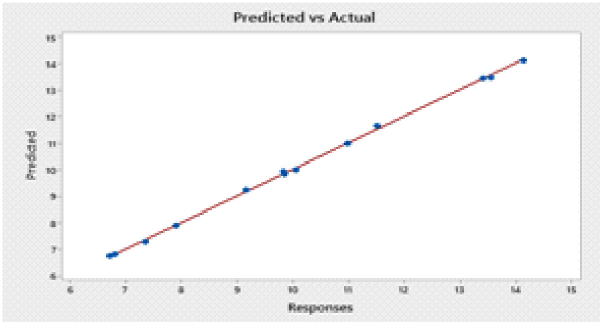
(a)



(b)



(c)



(d)

Figure 1: All Analytical 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 Nanoparticles

$$SnCl_2 + H_2O \rightarrow Sn^{+2} + 2Cl_2^- \quad (4)$$

$$NaOH \rightarrow OH^- + Na^+ \quad (5)$$

$$Sn^{2+} + 2OH \rightarrow Sn(OH)_2 \quad (6)$$

$$Sn(OH)_2 \rightarrow SnO + H_2O \quad (7)$$

$$SnO + H_2O \rightarrow SnO_2 + H_2 \quad (8)$$

Farrukh *et al*. (2010) had noted that a slow addition of sodium hydroxide through decomposition of urea improves the condensation of free Sn-Cl and Sn-OH species during the synthesis of SnO_2 nanoparticles, leading to a more fully condensed tin oxide framework and larger particle size. In the case of precursor concentration, low concentration of tin precursor reactants caused the reaction rate and the nucleation process to become slow which resulted in a broad size distribution of the SnO_2 nanocrystallites (Farrukh *et al*. (2010). In addition, the probability that growth units combined into crystal plane was also significant (Liu *et al*., 2014). Whereas high concentration of the tin precursor (0.40 mol/dm^3) at pH (10) when the synthesis temperature was held at (57.50°C), resulted in an increase in the reaction rate and nucleation process giving rise to tiny particles. The overall effect between these interactions is a decrease in the crystallite sizes of the SnO_2 nanoparticles formed.

In the Figure 3, the effect of interaction between the temperature and pH on the SnO_2 nanoparticles size as (3-D) Response Surface and (2-D) Contour Plot were evaluated. From both graphs, it was revealed that the minimum crystallite size of less than 7 nm was obtainable from the experiment when the precursor concentration is held at 0.375 mol/dm^3 and pH is at 10.0, while the reaction temperature is at 43.5-57.5°C. Whereas, for the largest crystallite size obtainable from the experimental runs, the pH was at 12 and the temperature about 90°C, occurring at a fixed concentration of 0.375 mol/dm^3. Therefore, at an alkaline solution pH, the crystal size decreased with decreasing temperature. According to Sui *et al*. (2010), well-crystallized SnO_2 occurred at relatively high temperatures due to higher surface energy. The reaction temperature affects not only the reaction

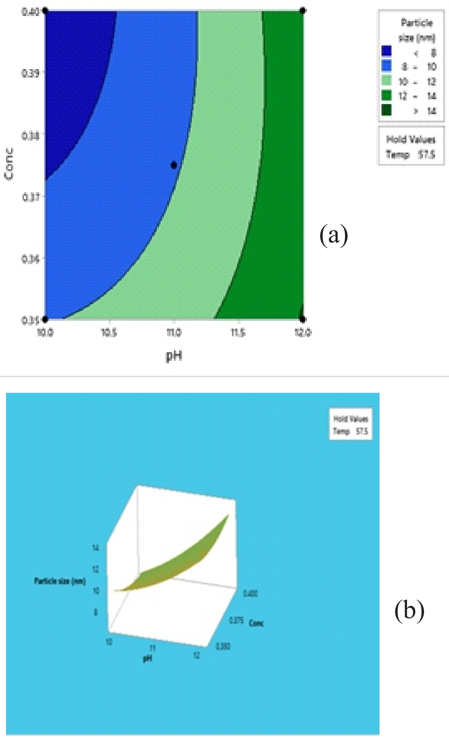


Figure 2: Effect of interaction between solution pH and precursor concentration on the SnO_2 nanoparticles size as (a) 2D contour plot and (b) 3D response surface.

rate, but also the growth and nucleation rates of the particles. Therefore, raising the reaction temperature within a specific range increases the diffusion, nucleation and growth rates.

Hence at an average temperature of 57.5°C, increasing the precursor concentration of SnO_2 from 0.350 to 0.40 mol/dm^3 over a pH of 10.2 results to a minimum crystallite size of less than 7 nm. On the other hand, the maximum crystallite size of 14 nm was obtained when the precursor concentration was varied between 0.350 to 0.40 mol/dm^3 at a pH of up to 11.8 at temperatures above. 57.5°C

It can be said that the pH of the reactant mixture and the synthesis temperature were considered to be significant factors that affected the size of the SnO_2 nanoparticles. Furthermore, Akhir *et al*. (2016) described the synthesis of tin oxide nanostructures using hydrothermal method and optimization of its crystal size by using statistical design of experiment. In the report, Akhir and his co-workers obtained nanostructures with smallest crystal size of 7.88 nm when precursor concentration was 0.16 M, at a treatment temperature of 120 °C and 12 h reaction time. On the other hand, the biggest crystal size of 18.41 nm was obtained at temperature of 180 °C, precursor concentration of 0.12 M and 12 h reaction time. The variation in the crystallite size obtained could be

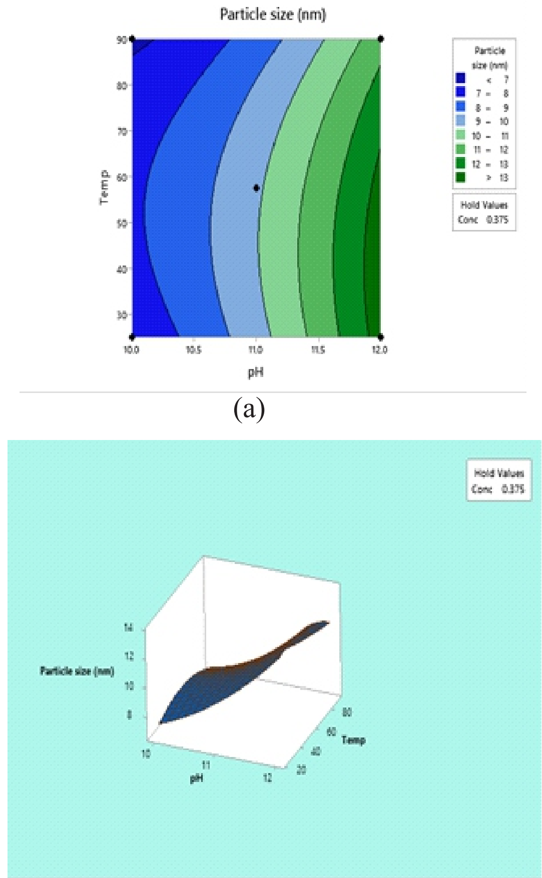


Figure 3: Effect of Interaction Between the Temperature and pH on the SnO_2 Nanoparticles Sizes as (a) 2D Contour Plot and (b) 3D Response Surface.

attributed to the difference in SnO_2 precursor, the variation in optimized synthesis parameters as well as the synthetic route adopted for the synthesis.

Characterization of the SnO_2 Nanoparticles.

In Figure 4, 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 Debye-Scherrer Equation (9). The average crystallite sizes were found to be 6.71 nm at pH 10.

$$D = \frac{0.93\lambda}{\beta \cos\theta} \tag{9}$$

where D is the crystallite size in (nm) β is the full with at half maximum (FWHM) of the diffracted peak, 0.93 is a constant, λ is the wavelength of the X-ray, and θ is the angle of diffraction in degrees.

Figure 5(a) shows agglomerated spherical shaped structures of SnO_2 at pH 10. The reason for this surface morphology can be explained in terms of OH^- and H^+ ions concentration in the reacting mixture. NH_4OH (the base solution) reacts with the precursor solution containing tin chloride and the plant extract leading to the formation of $Sn(OH)_2$ compound during the reaction process and later dissociates into Sn^{2+} and OH^- ions. When the concentration of Sn^{2+} and OH^- ions were more than the critical value, (Sn^{2+}) plays a major role in the formation of SnO_2 nuclei (Wahab, 2009). In basic medium (> pH 7) the OH^- ions interact with positively charged Sn^{2+} and form SnO_2. Consequently, at a higher pH of 10 hydrolysis and condensation took place and irregular shaped spheres were predominantly formed with more compact agglomeration as shown in Figure 5(b). Figure 5(c) represents the EDX spectrum of synthesized SnO_2 nanoparticles. The pattern illustrates the existence of

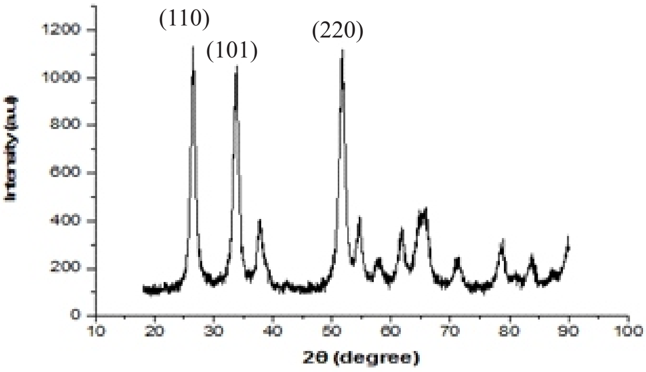


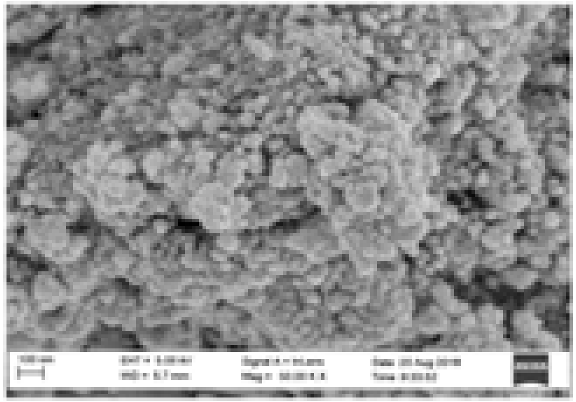
Figure 4: XRD Pattern for the SnO_2 Nanoparticles.

main constituents such as Sn and O. The existence of these atoms may confirm the formation of pure SnO_2 phase (Elango *et al*., 2015).

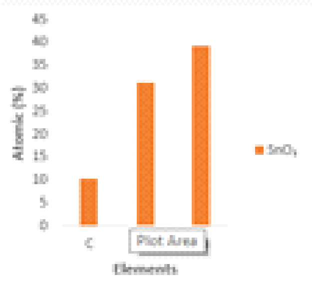
Comparison with OtherRrelated Studies

In general, Merlin *et al*. (2018) have reported the effects of factors such as temperatures and solution pH on the final size of SnO_2 nanoparticles, while Akhir *et al.* (2016) reported the effect of precursor concentration, calcination temperature and stirring time on the particle size of SnO_2 produced by hydrothermal synthesis. Consequently, the prediction of the particle size of SnO_2 was compared to the results of various other methods and summarized in Table 4. Relatively smaller particle size of SnO_2 was produced by green synthesis as compared to other methods.

This result exhibited the good and easy control of the particle size by controlling the rate of bio-reduction, hydrolysis and condensation reaction between the tin precursor and plant extracts. Nevertheless, in Table 5,



(a)



(b)

Figure 5: (a) HRSEM (b) EDX of SnO_2 Synthesized at pH 10, Concentration of 0.4 M and 57.5°C.

the optimization of different process parameter via the Box-Behnken Design resulted to a high correlation values (R^2 and R^2_{adj} for both NiO and SnO_2) regardless of the method of synthesis. Hence, the optimization of the experiment with Box-Behnken Design as a statistical tool brought about flexibility in manipulating the sizes of SnO_2 nanoparticles. Therefore, this method can also be scaled up to predict more responses such as shape and distribution of the nanoparticles for more economical feasibility in the production of metallic oxide nanoparticles. in the future.

CONCLUSION

The production of SnO_2 nanoparticles using green synthesis was well accomplished 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 nanoparticles. It was observed that the solution pH had most significant effect on crystal size trailed 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 such as solution pH and precursor concentration. As important factors that governs the reaction mechanism in forming

Table 4: Preparation of SnO_2 NPs using different methods with **their** particle sizes.

No	Method	Particle size (nm)	Application of DOE	References
1	Sol-gel	8.50	No	Riaz *et al.* (2013)
2	Sol gel	9.23	No	Suhai *et al.* (2014)
3	Green Synthesis	4.00	No	Elango *et al.* (2015)
4	Co-precipitation	14.10	No	Nadaf and Venkatesh, (2016)
5	Hydrothermal	13.12	Yes (Cube plot)	Akhir *et al.* (2016)
6	Green Synthesis	17.5	No	Selvakumari *et al.* (2017)
7	Precipitation	32.15	No	Merlin *et al.* (2018)
8	Green Synthesis	2.60	No	Sunny, and Venkat, (2019)
9	Precipitation	20.40	No	Mevada *et al.* (2020)
10	Green Synthesis	10.09	Yes (Box-Behnken)	Present study

Table 5: Preparation and optimization of metallic NPs with the Box-Behnken Design

No	Metallic Nanoparticles	Method	Optimized dependent variable	Response(s)	ANOVA data	References
1	NiO	Sol-gel	Solution pH (1.02), Molar ratio (1:1.74) and Calcination temperature (400.08°C)	Particle size (14.31 nm)	(R^2= 0.9859 R^2_{adj}=0.9677)	Ba-Abbad *et al.* (2015)
2	Ag	Green synthesis	Concentration of $AgNO_3$ (0.05 M), synthesis temperature (70°C) and volume of plant extract (2 cm^3).	Particle size (98 nm) and Polydispersity Index (0.15)	Not provided	Hasnain *et al.* (2019)
3	SnO_2	Green synthesis	Solution pH (10), precursor concentration (0.40 M), and synthesis temperature (57.5°C).	Particle size (6.71 nm).	R^2 = 0.9996, $R^2_{(adj)}$ = 0.9987, $R^2_{(pred)}$ = 0.9928	Present study

nanoparticles. Further studies are recommended for the investigation of other response factors such as the shape and distribution of nanoparticles with respective to the solution pH, precursor concentration and synthesis temperature as process parameters by means of optimization with experimental designs.

REFERENCES

Akhir, M. A. M., Mohamed, K., Lee, H. L. and Rezan, S. A. (2016). "Synthesis of Tin Oxide Nanostructures using Hydrothermal Method and Optimization of its Crystal Size by Using Statistical Design of Experiment " *Pro. Chem.*, 19:993-998. https://doi.org/10.1016/j.proche.2016.03.148.

Alaoui, A., Kacemi, K. E. L., Ass, K. E. L. and Kitane, S. (2015). "Application of Box-Behnken Design to Determine the Optimal Conditions of Reductive Leaching of Mno_2 from Manganese Mine Tailings." *Russ. J. Non-Ferr. Met.*, 56:134-141.

Ba-abbad, M. M., Chai, P. V., Takriff, M. S., Ben, A. and Mohammad, A. W. (2016). "Optimization of Nickel Oxide Nanoparticles Synthesis Through the Sol-Gel Method using Box–behnken Design". *Mat. Des.*, 86:948-956. https://doi.org/10.1016/j. matdes.2015.07.176.

Ba-Abbad, M. M., Kadhum A. A., Mohamad, A. B, Takriff, M. S. and Sopian, K. (2013). "Optimization of Process Parameters using D-Optimal Design for Synthesis of ZnO Nanoparticles via Sol–gel Technique." *J. Ind. Eng. Chem.,* 19:99-105.

Chopra, K. L., Major S. and Pandya D. K., (1983). "Transparent Conductors". *T. S. Films,* 102:1-46.

Courchesne N. M. D., Klug M., Chen P. Y., Kooi S. E., Yun D. S., Hong N., Fang N. X. and Belcher A. M. (2014). "Assembly of a Bacteriophage-Based Template for the Organization of Materials into Nanoporous Networks". *Adv. Mater.,* 26:3398-3404.

Elango, G., Manoj, S., Santhosh, S., Muthuraja, S. and Mohana, S. (2015). "Green Synthesis of SnO_2 Nanoparticles and its Photocatalytic Activity of Phenol-Sulfonphthalein Dye". *Spect. Act Part A: Mol. Bio. Spec.,* 145: 176–180. https://doi.org/10.1016/j.saa.2015.03.033.

Farrukh M.A., Heng B. and Adnan R. (2010). Surfactant-Controlled Aqueous Synthesis of SnO_2 Nanoparticles via the Hydrothermal and Conventional. *Turk. J. Chem.*, 34:537-550.

Hasnain, M. S., Javed, N., Alam, S. and Rishishwar, P. (2019). "Purple Heart Plant Leaves Extract-mediated Silver Nanoparticle Synthesis: Optimization By Box-Behnken

Design. *Mat. Sci. Eng. C. 99*(1):1105–1114. https://doi.org/10.1016/j.msec.2019.02.061.

Jafarzadeh, N. K., Sharifnia, S., Hosseini, S. N. and Rahimpour, F. (2011). Jafarzadeh N. K, Sharifnia S, Hosseini S. N, Rahimpour F. Statistical Optimization of Process Conditions for Photocatalytic Degradation of Phenol with Immobilization of Nano TiO_2 on Pearlite Granules". *Kore. J. Chem. Eng.,* 28:531-538.

Kalubarme, R. S., Lee J. Y. and Park C. J. (2015). "Carbon Encapsulated Tin Oxide Nanocomposites: An Efficient Anode for High Performance Sodium-Ion Batteries". *ACS Appl. Mater. Inter.*, 7:17226-37.

Kamaraj, P. Vennila, R. Arthanareeswari, M. and Devikala, S. (2014). Biological Activities of Tin Oxide Nanoparticles Synthesized Using Plant Extract. *World. J. Pharm. Pharmaceut. Sci*., 3(9):382-388.

Liu, D., Liu Y., Zong, R., Bai, X. and Zhu, Y. (2014). "Controlled Synthesis of 1D ZnO Nanostructures via Hydrothermal Process". *Mat. Res. Bull.*, 49 (1):665-671.

Merlin, C., Vedhi, K., Muthu, A. and Mohamed, S. (2018). "Influence of pH and Temperature on the Structure and Size of Tin Oxide Nanoparticles". *J. Nano. Tech.*, 4(5):564–566.

Mevada, C., Chandran, P. S. and Mukhopadhyay, M. (2020). Room-temperature Synthesis of Tin Oxide Nanoparticles using Gallic Acid Monohydrate for Symmetrical Supercapacitor Application. *J. Energ. Sto.*, 28:101197. https://doi.org/10.1016/j.est.2020.101197

Minami, T. (2000). "New n-Type Transparent Conducting Oxides" *MRS Bull.*, 25:38-44.

Nadaf, L. I. and Venkatesh, K. S. (2016). Synthesis and Characterization of Tin Oxide Nanoparticles by Co-precipitation Method. *IOSR J. Appl. Chem. (IOSR-JAC)*., 9(2):01-04

Oluwafemi, O. S., Lucwaba, Y., Gura, A., Masabeya, M., Ncapayi, V., Olujimi, O. O. and Songca, S. P. (2013). "A Facile Completely 'Green' Size Tunable Synthesis of Maltose-reduced Silver Nanoparticles Without the Use of any Accelerator". *Coll. Sur. B: Biointers.*, 102:718–723. https://doi.org/10.1016/j.colsurfb. 2012.09.001.

Phindile, B. K, Makwena, J. M. and Lucky, M. S. (2012). "The Effect of Solvents, Acetone, Water, and Ethanol, on the Morphological and Optical Properties of ZnO Nanoparticles Prepared by Microwave". *J. Nanotechnol*., 195106 -195112.

Rauf, M. A., Marzouki, N. and Korbahti, B. K. (2008). "Photolytic decolorization of Rose Bengal by UV/H_2O_2 and data optimization using response surface method". *J Haz. Mater.,* 159:602-609.

Riaz, S, Nairan, A. and Naseem, S. (2013). Synthesis and characterization of SnO_2 Nanoparticles for PV Applications. *Adv. Nano. Bio. Robo. Ene Res.,* 25(28):296-301.

Selvakumari, J. C, Ahila, M, Malligavathy, M. and Padiyan, D, P. (2017). Structural, Morphological, and Optical properties of tin (IV) oxide nanoparticles synthesized using *Camellia Sinensis* Extract: a Green Approach. *Inter. J. Min. Metall. Mat.,* 24(9):1043-1048 DOI: 10.1007/s12613-017-1494-2.

Senthilkumar, S., Perumalsamy, M., Prabhu, H. J., Basha, C. A. and Swaminathan, G. (2013). "Box Behnken Design-based Optimization of Solar Induced Photo Catalytic Decolourization of Textile Dye Effluent". *Cent. Eur. J. Eng.,* 3:135-144.

Shang, G., Wu J., Huang M., Lin J., Lan, Z., Huang Y. and Leqing F. (2012). "Facile Synthesis of Mesoporous Tin Oxide Spheres and Their Applications in Dye-Sensitized Solar Cells". *J. Phys. Chem.* C., 116:20140- 20145.

Sharghi, H., Ebrahimpourmoghaddam S., Memarzadeh R. and Javadpour S. (2013). "Tin xide Nanoparticles (NP-SnO_2): Preparation, Characterization and their Catalytic Application in the Knoevenagel Condensation". *J. Iran. Chem. Soc.,* 10:141- 149.

Sharmila, G., Muthukumaran, C. and Sangeetha, E. (2019). "Characterization of *Pisonia alba* leaf extract derived MgO Nanoparticles and its Biological Applications". *Nano-Stru. Nano-Objs.*, *20*: 100380. https://doi.org/ 10.1016/ j.nanoso.2019.100380.

Sudhaparimala, S., Gnanamani A. and Mandal A. B. (2014). "Green Synthesis of Tin Based Nano Medicine: Assessment of Microstructure and Surface Property". *J. Nanosci. Nanotechnol.,* 2:75-83.

Suhail, A. M., Naje, A. N., Muhammed, G. S. and Norry, A. S. (2014). Synthesis and Characterization of SnO_2 Nanoparticles UV-Photoconductive Detector. *Inter. J. Cur. Eng., Tech.* 4(5):3610-3613.

Sui, Y., Fu W. and Yang H. (2010). "Low Temperature Synthesis of Cu_2O Crystals: Shape Evolution and Growth Mechanism". *Cryst. Growth Des.,* 10(1):99-108.

Sunny, N. E. and S, V. K. (2019). Biogenesis, Characterisation and Bio-efficacy of Tin Oxide Nanoparticles from *Averrhoa Bilimbi* Fruit Extract. *Int. J. Recent Tech. Eng*., 8(4):10309–10315. https://doi.org/10.35940/ijrte. D4523.118419

Wahab, R., Kim, Y. S. and Shin, H. S. (2009). "Synthesis, Characterisation and Effect of pH Variation on Zinc Oxide Nanostructures". *Mat. Trans.,* 50(8):2092–2097.

Yan, T. J. Wang, X. X., Long, J. L., Liu, P., Fu, X. L., Zhang, G. Y., and Fu, X. Z. (2008). Urea-based Hydrothermal Growth, Optical and Photocatalytic Properties Of Single Crystalline $In(OH)_3$ Nanocubes, *J. of Colloid. Inter. Sci.*, 325:425-431.