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PHYTOCHEMICAL SYNTHESIS, CHARACTERISATION AND SIZE OPTIMISATION OF COPPER NANO PARTICLES FOR METAL CUTTING COOLANT APPLICATIONS

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Abstract

Copper nano particles have been successfully synthesised through phytochemical synthesis in this study. The average particle size has been measured and optimized utilizing the Response surface methods (RSM). The particles size distribution results revealed a range of values between 70.11nm and 100.77nm based on the particles percentage intensity and the UV-VIS spectroscopy confirmed the formation of copper nano particles at a surface plasmon of 520nnm. The optimum particle size has been determined to be [redacted] *81.45nm within the range of values considered in this study.*

KEYWORDS:
Copper, Metal, Synthesis, Coolant, Particles.

Introduction

Traditionally, several physical and chemical synthesis techniques have been used to synthesize nanoparticles. These techniques include: sol-gel, laser ablation, microwave-assisted process, co-precipitation, pulsed wire discharge, vacuum vapor deposition, high-energy irradiation, lithography, mechanical milling, photochemical reduction, electrochemistry, electrospray synthesis, hydrothermal reaction, micro emulsion, and chemical reduction (Din et al. 2017). However, due to its low toxicity, comparatively low cost, eco-friendliness, and better biocompatibility, green synthesis has been gaining grounds in the domain of nano particles synthesis in recent times. Green synthesis focuses on the development of nano particles with a view to averting hazards

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experienced from chemical toxicity, energy conservation, waste reduction, sustainability and life cycle considerations (Chokkareddy and Redhi, 2018). These are important distinctions targeting environmental safety which is one of the major focal points of nanotechnology.

Nano particles are defined as particles with size ranging from 1 nanometers (nm) to 100 nm in length in at least one dimension (Hutchison, 2008); exhibiting improved properties based on specific characteristics such as size, distribution and morphology. Nano particles are classified as metallic nano particles such as Copper, Aluminum, Zinc, Nickel, Silicon, Iron, Titanium, Gold and Silver) and non-metallic nano particles such as Aluminum oxide, Copper oxide, Zinc Oxide, Titanium Oxide, Silicon carbides, carbon nanotubes and composites/core polymer shell composites (Sreejith and Ngoi, 2000, Yu and Xi, 2012, Ozerinc *et al.* 2010).

Copper has been reported to have up to 700 times higher thermal conductivity than water (Shokoohi and Shekarian, 2016). The availability of Copper, it's cheaper cost when compared with other expensive noble metals such as Gold and Silver, its good thermal and high electrical conductivity makes it a potentially applicable material in the development of nanofluids which are used as cooling fluids for electronic systems, metal cutting operations and cooling in heat exchangers (Loulijat et. Al. 2015). High thermal conductivity nanofluids are always targeted for cooling objectives. Hence, when metallic nano particles like copper are added to a basefluid for the purpose of cooling, the overall thermal conductivity of the coolant improves tremendously. The thermal stability of copper nano particles increases with increase in nano particle size (Oleg *et al.* 2008 and Loulijat et al. 2015).

In phytochemical or green synthesis of nanoparticles, bioactive components identified in plant extracts act as both stabilizing (capping) and reducing agents throughout the process. These bioactive components include: polyphenols, alkaloids, proteins, sugars, phenolic acids, and terpenoids. Some plants which possess such capability include: Aloe Vera, elephant grass, mango leaves, tea leaves, lemon grass, neem leaves to mention a few. Ramadas and Subramanian (2018) have conducted a phytochemical screening of neem plant in three different solvents (aqueous, ethanol and chlorofoam) and their results revealed bioactive components. Neem leaves have been chosen as the source of reducing agent in this study due to its wide availability and potential bioactive components.

Green synthesis of nanoparticles proceeds in three phases, namely activation phase, growth phase and termination phase. In the activation phase, metal ions

are recovered from their salt precursors by the action of plant metabolites which have metal reduction abilities. These metal ions are further transformed from their monovalent/ divalent oxidation states to zero valent states. This process is followed by the nucleation of the reduced metal atoms. These atoms connect together to form metal nano particles as further reduction of the metal ions continues into the growth phase. In the growth phase, nanoparticles join to form an assortment of morphologies such as cubes, spheres, triangles, hexagons, pentagons, rods, and wires. In the termination phase, the nanoparticles eventually achieve their maximum activity and permanent morphology.

Plant extract concentration plays a key role in reducing and stabilizing the CuNPs. Increasing the concentration of the plant extract increased the concentration of the phytochemicals present in the extract thereby increasing the rate of reduction of the copper salt leading to increased number of particles (Daniel et. al. 2013). Similarly, smaller-sized nanoparticles are obtained at high pH (basic range) as opposed to those obtained at low pH (acidic range). Additionally, required particle size and shape is usually achieved through optimization (adjustment of the appropriate reaction parameters) of the synthesis process.

Nanomaterials are generally characterized by carrying out Ultra Violet–Visible (UV-VIS) Absorption Spectroscopy, Fourier Transform Infrared Spectrum Analysis, X-ray Diffraction and microscopic techniques such as transmission electron microscopy (TEM) scanning electron microscopy (SEM), atomic force microscopy and nano indentation (Shobha *et al*. 2014, Nayak *et al*. 2016)).

MATERIALS AND METHODS

Materials

The following materials were used during the Phytochemical synthesis of copper nano particles.

i. 20g of Neem leaves
ii. Morning fresh detergent
iii. Pair of scissors
iv. Folin-Denis' reagent
v. 17.8g of Copper II chloride ($CuCl_2$) powder
vi. 100ml of Di-ionised (DI) water
vii. 10ml of neem leaves extracts
viii. 200ml beaker, 500ml beaker, 400ml measuring cylinder
ix. Whatman filter paper No 1.

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x.Hand gloves
xi.Sieve (50mm ×ϕ110mm)
xii.Eye googles

Equipment

i. Crown Star Electric Stove (1500W capacity)
ii. weighing balance (Model: Scout Pro SPU 402, made in china)
iii. Double beam Shimadzu UV-spectrophotometer, UV-1800Shimadzu
iv. High resolution Bench pH metre (Model No. pH 213).
v. Reflux Apparatus (condenser and 500ml flask)
iv. High Speed Refrigerating Centrifuge, Model N0: LR-16A
v. Drier Box, AX- 0V 73
vi. Zeta sizer, version 7.01

Synthesis Procedure and Characterization

The phyto chemical synthesis of copper nano particles and characterization has been done in the following sequence: collection of neem leaves, preparation of reducing agent from Neem leaves, Synthesis of Copper Nano Particles and Characterisation. These processes are detailed as follows.

a. Collection of Neem Leaves

Healthy and fresh leaf samples were selected from around the premises of Federal University of Technology, Minna (Bosso Campus). Leaves from different cultivars were kept separately. These were placed in dry paper bags and labelled. Leaves were washed with water and subsequently washed gently in a domestic detergent -Morning Fresh. The leaves were thereafter rinsed with over flowing tap water. These were further rinsed with distilled water, and the leaves moisture allowed to dry out for 3 hours. The leaves were further cut with the aid of a pair of scissors to ensure that the required quantity of the leaves is contained in the 500ml capacity beaker.

b. Preparation of reducing agent from Neem leaves

20 grams of the cut neem leaves was weighed with the aid of a weighing balance (Model: Scout Pro SPU 402, made in china). The weighing balance is shown in Figure 3. 100ml of de-ionised water was measured using a measuring cylinder (400ml capacity) and added to 20g of the cut neem leaves placed in a beaker (500ml capacity). The beaker was then placed in a pot filled to its two-thirds with

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water. This was subsequently placed on a Crown Star electric stove and heated at 80°C until it began to boil (Figure 4). The boiling began at approximately 9 minutes, marking the beginning of boiling of the neem leaves. Boiling was maintained for 15 minutes after which the electric stove was switched off. This mixture was subsequently cooled and filtered using the Whatman filter paper no. 1. The resulting aqueous extract is the reducing agent. The resulting extract was stored in a refrigerator until its use. This reducing agent was used for green synthesis of copper nano particles. This was adapted from Keihan *et al.* (2016). Similar extraction was carried out for 20g, 25g and 30g of neem leaves using the same quantity of de-ionised water.

c. Synthesis of Copper Nano Particles

10ml of the prepared reducing agent (with an adjusted pH of 10) was added to 100ml of a prepared 1mM aqueous copper chloride ($CuCl_2$) solution (placed in a round bottom flask) which in turn was placed in a heating mantle and refluxed at 100°C for 3 hours as shown in Figure 5. The emerging solid precipitate solution was allowed to cool and poured into plastic tubes for Centrifuging in order to separate the precipitate from the solution. The resulting precipitate was washed thoroughly and dried in the oven at 80°C for 12 hours, leaving the nano powder at the bottom of the beaker. The resulting copper nano particles (in powder form) was stored appropriately in a labelled container for particle size analysis (adapted from Keihan et al. 2016). This procedure was repeated for various weights of neem leaves (20g, 25g and 30g) and centrifuged at 10,000rpm.



Figure 3: Weighing balance Scout Pro SPU 402



Figure 4: Set up for reducing agent preparation

(Drugs Delivery Laboratory, CGEB, Federal University of Technology, Minna)

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Figure 5: A Reflux Apparatus Set up in a Heating Mantle
(Drugs Delivery Laboratory, CGEB, Federal University of Technology, Minna)





Figure 6: High Speed Refrigerating Centrifuge Model No: LR-16A
Figure 7: A Drier Box, AX- 0V 73
(Drugs Delivery Laboratory, CGEB, Federal University of Technology, Minna)

d. Characterisation

The UV-VIS spectroscopy and Particle size determination have been done in this study with the help of the Shimadzu UV-spectrophotometre UV-1800 and a zetasizer, ver 7.01.

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Figure 8: Shimadzu UV-spectrophotometer UV-1800



Figure 9: Zeta sizer ver. 7.01

(Drugs Delivery Laboratory, CGEB and Nanotechnology Laboratory, CGEB, FUT, Minna)

f. Design of Experiments (DOE)

In developing copper nano particles, statistical design of experiments technique has been invoked. It is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Yusuf and Riza, 2005). Some major types of design of experiments include: full factorials, fractional factorials, screening experiments, mixture experiments, response surface methods. There are two types of Response surface designs namely the Face Centered Design (FCD) and the Central Composite Design (CCD). The CCD for k = two factors has been utilized in this study. This is shown in Figure 2.

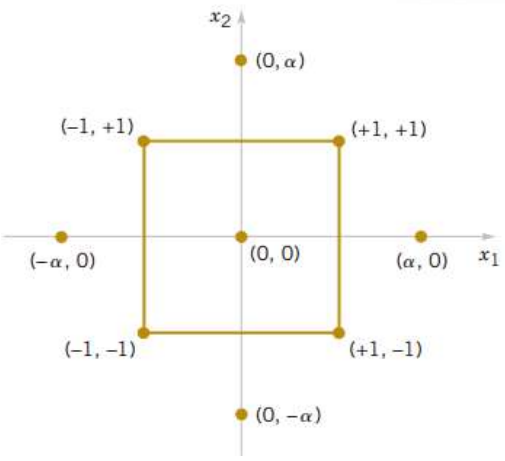

Figure 10: Central Composite Design for two factors, k = 2 (Montgomery and Runger, 2003)

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Central composite design (CCD) is the most popularly adopted design for fitting a second order model. For second order model parameters to be successfully evaluated, an experimental design consisting of three levels for each factor has to be used. This involves a 2^k factorial (coded as ±1 notation) strengthened by 2k axial points (+α, 0, 0, ,0), (0, ± α 0, ,0), (0, 0, ±α, 0), (0, 0, 0, ±α) and n_0 centre points (0, 0, 0).

RESULTS

This section reports the results of the synthesis copper nano particles and optimization of particle size. Table 1 shows the conditions and experimental design utilized in screening the most important factors for subsequent optimization of nano particles size in this study and Table 2 shows the analysis of variance (ANOVA)

Table 1: Experimental Screening Design showing the factors and the measured Response

Dispersant name: water Dispersant Refractive Index :1.330 Viscosity (cP):0.8872

Material Refractive Index :1.59 Material absorption: 0.010

Standard	Run	Block	Factor A: pH	Factor B: Broth concentration(%)	Factor C: Reaction Time (Hours)		Factor D: Incubation Temperature (Degrees celcius)	Response (Nanometres)
1	6	1	10	0.20	3.0		100	86.04
2	5	1	11	0.20	3.5		100	84.49
3	1	1	10	0.30	3.5		100	85.51
4	4	1	11	0.30	3.0		100	79.81
5	2	1	10	0.20	3.5		110	77.07
6	3	1	11	0.20	3.0		110	75.63
7	7	1	10	0.30	3.0		110	76.85
8	8	1	11	0.30	3.5		110	71.49

Table 2: Analysis of Variance Table

Source	Sum of squares	df	Mean Squares	F value	p-value prob>F	
Model	187.59	4	48.93	1200.93	<0.0001	Significant
A-pH	24.68	1	3.3	81.61	0.0029	
B-Broth. Conc.	11.45	1	7.23	177.46	0.0009	
C-Inc. Temp.	151.47	1	151.47	3717.36	<0.0001	
AB	8.14	1	8.14	199.79	0.0008	
Residual	0.12	3	0.041			
Cor Total	195.85	7				

a. UV-VIS Spectroscopy Spectrum Peak Results

The UV-VIS Spectroscopy spectrum peak result shows the peak wavelength values at which the copper nano particles were formed. Figure 10 shows the UV-VIS Spectroscopy of copper colloid synthesized at pH =10.36, Reaction Incubation Temperature of 106.2 °C. Points marked 1-4 on Figure10 indicate the peak values of 506nm ,554.80nm ,771nm and 784nm obtained for copper nano particles while points 6,7,8 indicate the valleys of 788nm,775nm and 536nm. These all fall within the absorption wavelength of copper nano particles which ranges between 550nm and 800nm.

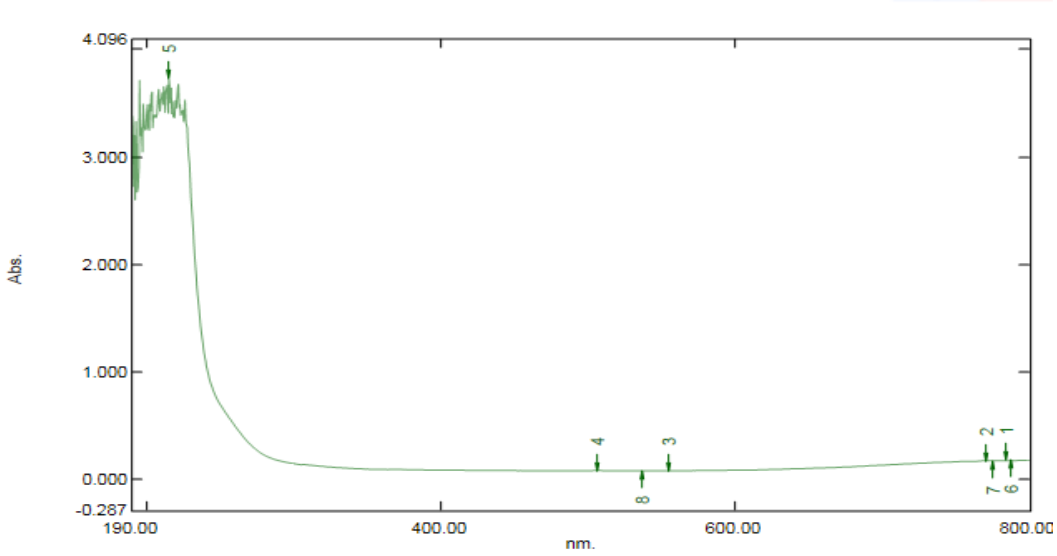

Figure 11: UV- VIS spectroscopy of Copper colloids synthesised at a pH =10.36, Incubation Temperature of 106.2 °C.

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b. Analyses of Results in Design Expert Software

The design expert software version 7.0.1 has been used to carry out all the analyses in this study. Figures 12 and 13 show the half normal plot of the factors and the Pareto chart of the effects respectively.

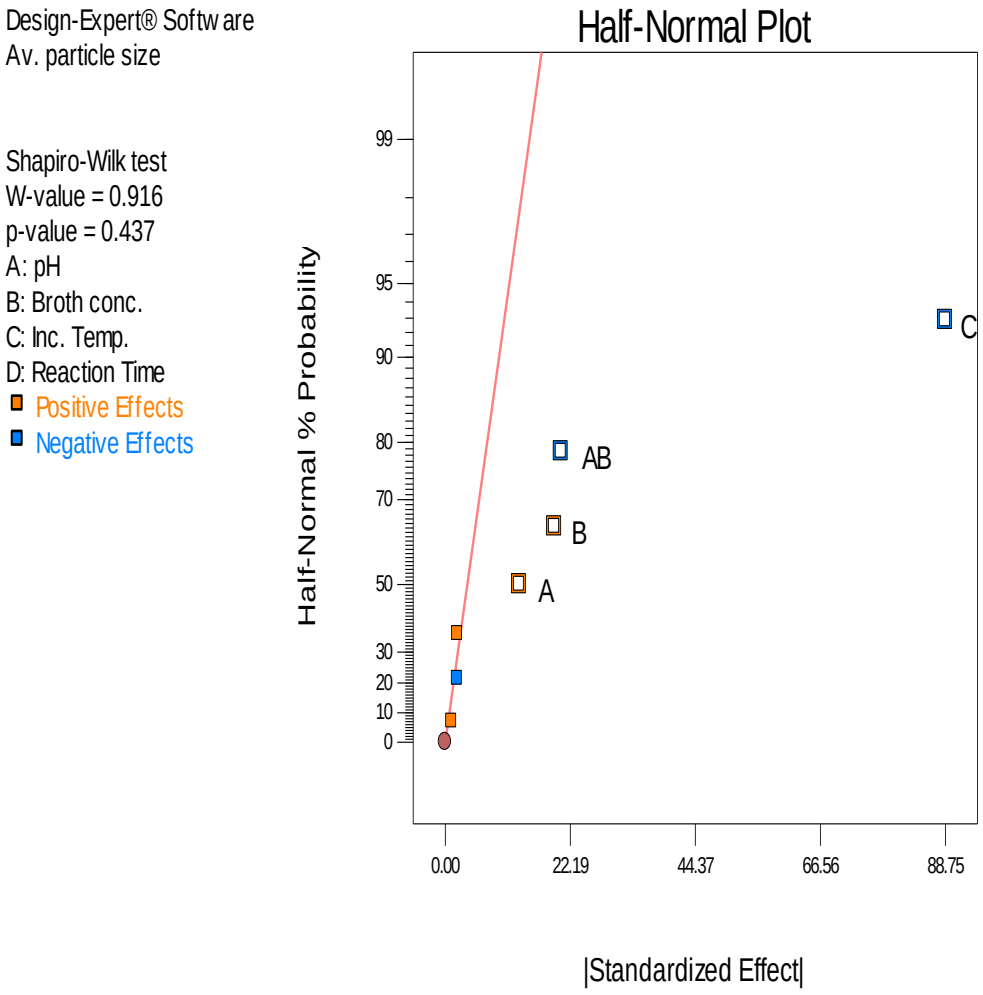

Figure 12: Half Normal Plot of the effects

c. Discussion of Half Normal plot Result

The significant effects with the largest absolute values show at the upper right hand corner. A rapid deflection of the line towards the left shows a transition between the significant and insignifant effects when effects are being selected. These effects are more clearly illustrated in the Pareto plot as shown in Figure 12.

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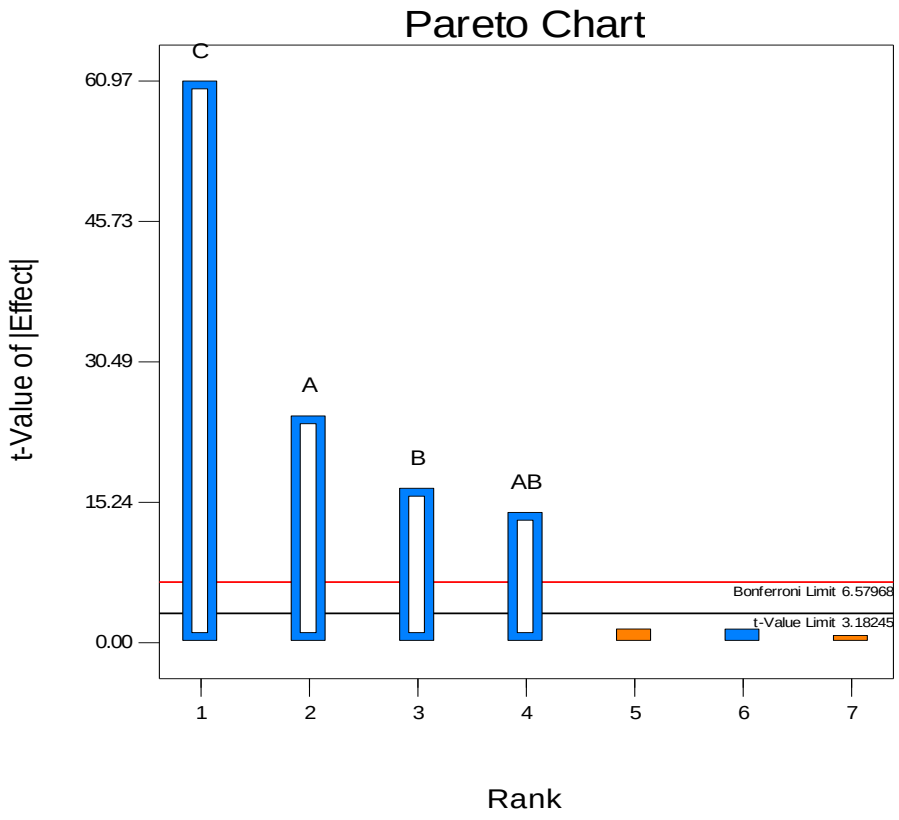

Figure 13: Pareto Chart of the effects

d. Discussion of Pareto Chart

Factors C, A, B and their interaction AB have passed both the Bonferroni line and t-value line indicating that these factors have the main effects on the particle size. Hence these factors have been included in the eqaution. Other factors failed to pass both lines hence have been excluded from the equations.

e. Equations

The final equation in terms of coded factors:

Av. particle size = +107.93 +6.57 × A+399.75 × B-0.87 × C-40.35 × A × B

The final equation in terms of actual factors:

Av. particle size = +107.93125+6.57500 × pH+399.75000 × Broth conc. -0.87025 × Inc. Temp. - 40.35000 × pH × Broth conc.

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d. Experimental Design Utilising Response Surface Methods

The Central Composite Design for 2 factors (k = 2) consists of three levels for each factor with 7 added centre points. This design is shown in Figure 9 with measured response.

Table 3: Central Composite Design for two factors and measured response

Standard	Run	Block	Factor 1: pH	Factor 2: Incubation Temperature (Degrees Celsius)	Response1: Av. Particle Size (Nanometres)
1	3	1	10.60	104	70.11
2	6	1	10.20	106	75.50
3	5	1	10.60	102	76.25
4	10	1	10.80	104	76.99
5	13	1	10.60	106	79.81
6	1	1	10.40	108	86.04
7	9	1	10.60	106	86.07
8	4	1	10.60	106	87.11
9	8	1	10.80	108	90.17
10	12	1	10.60	106	91.70
11	7	1	10.60	106	92.65
12	2	1	11.00	106	93.42
13	11	1	10.60	110	100.70

e. Standard Error of Design

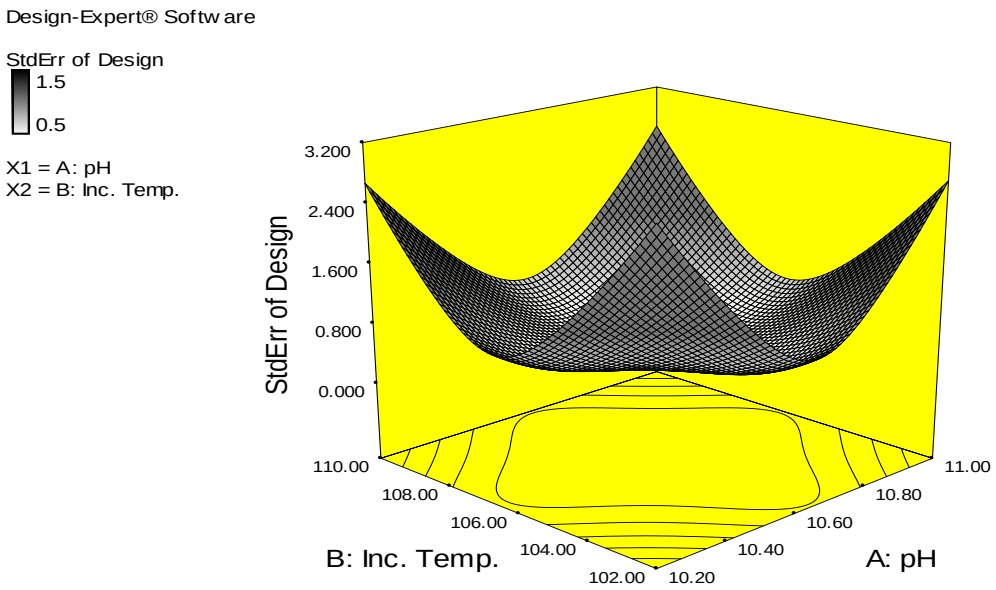

Figure 14: Design Evaluation Graph in 3-D plot.

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f. Numerical Optimisation

Figures 15 and 16 show the numerical optimisation graphs in 2D and 3D for the optimum average particle size.

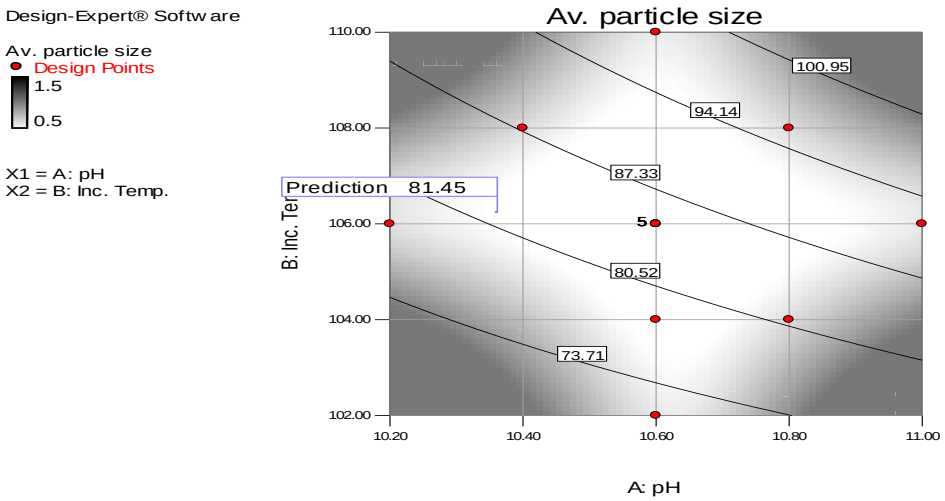

Figure 15: Numerical Optimisation graph in 2D

Based on the set of criteria adopted in this research with the goals of maximising the particle size (response), minimising the pH (factor A) and minimising the Incubation temperature (factor B), an optimum particle size of 81. 45nm has been obtained as shown in Figures 15 and 16.

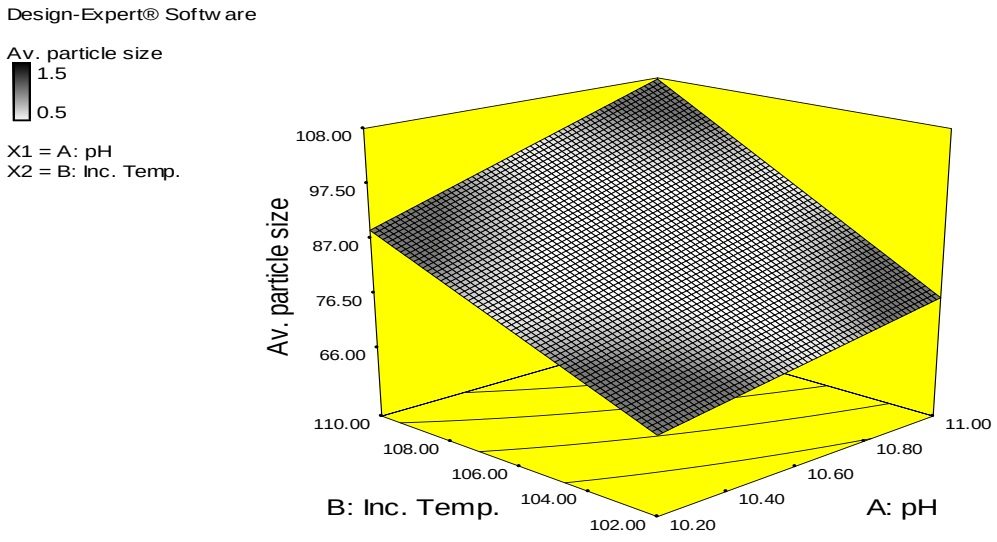

Figure 16: Numerical Optimisation graph in 3D

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CONCLUSIONS

From this study, the following conclusions can be drawn:

(i) Copper nano particles can be synthesised from copper II chloride powder and neem leaves extract when proper adjustment of the reaction parameters such as pH of the extract (from acidic to basic range) and the incubation temperature is made.

(ii) Characterisation of the phyto-chemically synthesised copper nano particles can be accurately achieved by UV-VIS spectroscopy and Particle Size Measurement.

(iii) Response Surface Methods has been effectively utilised for the optimisation of the average particles size and an optimum average particle size of 81.45nm has been obtained.

REFERENCES

Chokkareddy R. and Redhi G. (2018). Green Synthesis of Metal Nanoparticles and its Reaction Mechanisms. Electroanalytical Laboratories, Department of Chemistry, Durban University of Technology, Durban, South Africa. DOI: 10.1002/9781119418900.ch4.

Daniel SK, Vinothini G, Subramanian N, Nehru K, Sivakumar M. (2013). Biosynthesis of Cu, ZVI, and Ag nanoparticles using Dodonaea viscosa extract for antibacterial activity against human pathogens. J. Nano Res.

Keihan H.A., Veisi H., and Veasi H. (2016). Green synthesis and characterization of spherical copper nano particles as organo metallic anti-bacterial agent. Applied organometallic chemistry. pp 1-7.

Loulijat H., Zerradi H., Mizani S., Achhal E., Dezairi A. and Ouaskit S. (2015). The behavior of the thermal conductivity near the melting temperature of copper nano particle. *Journal of Molecular Liquids. Pp 695-704.*

Montgomery, D.C. and Runger, G.C (2003). Applied Statistics and Probability for Engineers", 3rd Edition, John Wiley and Sons, Inc., New York, USA, Pp.521, 620-622,675.

Oleg, A.Y., Igor, M.D., Alexander, A.A. and Andriy, M.D. (2008). Size dependent Meltingof Spherical copper nano particles. arXiv: cond-mat/0701276v1(cond-mat.mtrl-sci). pp 1-16.

Ozerinc, S., Kakac, S., and Yazicioglu, A.G., (2010). Enhanced thermal conductivity of nanofluids: a state-of-the-art reviewll, Microfluidics and Nano fluidics, 8, Pp 145–170.

Shokoohi Y., Khosrojerdi E., and Rassolian Shiadhi B.H. (2015). Machining and ecological effects of a new developed cutting fluid in combination with different cooling techniques on turning operation*, J. of Cleaner Prod. 94 Pp 330-339.*

Sreejith P.S. and Ngoi B.K.A (2000). Dry machining: Machining of the future, *Journal of Materials Processing Technology,*101, Pp287–291.

Yu W. and Xie H. (2012). A review on nanofluids: preparation, stability mechanisms, and applications. *Journal of Nanomaterials*, vol. 2, *Article ID 435873*, Pp 14-17.

Yusof, S. and Riza, A. (2005). Surface roughness model for machining mild steel with coated carbide tool. *Journal of Materials and Design*, pp 321-326.