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Comparative Modeling Approach Upon Synthesizing Silver Nanoparticles From *Solanum virginianum*

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ABSTRACT

The major objective focusses on synthesizing silver nanoparticles (Ag-NPs) from *Solanum virginianum* under optimum conditions. In this study, mathematical tools such as central composite design (CCD) and artificial neural networking (ANN) used for identifying process optimizing parameters. The maximum wavelength recorded (λ=425 nm) using chemical mediated synthesis for the leaf extract. Based on the results, that plant extract concentration (15 g ml^{-1}), temperature (65°C), time (11 mins) with pH (13) yielded the highest concentration 2mg g^{-1} of Ag-NPs. Furthermore, the statistical analysis yielded regression coefficient (R^2) showing 0.96 indicating the RSM model & ANN model is in similar with the obtained investigational results. Interaction effect shows that plant extract concentration, time and pH were significant with $p<0.05$.

Keywords: *Solanum virginianum,* AgNPs, RSM, ANN.

INTRODUCTION

Advanced material such as metal derived nanoparticles have extensive applications due to its unique surface properties[1-4]. There are various techniques for producing silver nanoparticles viz, chemical route, photoreduction in reverse micelles[5-10].Since nanoparticles are used widely for applications that necessitates for emergent aneco-friendly and cost-effective process[11]. The biological sources (microbial and plantbiomass) could be a substitute approaches for nanoparticles synthesis in an eco-friendly manner[12]. However, plant route is more advantageous due to the painstaking maintenance of microbial cultures[13]. Hence plant route attracted the scientific community toidentify potential sources and its applications. For instance, plant sources

such as *Alfalfa, Aloe vera, Cinnamon camphora, Carica sp, Parthenium hysterphorrus, Diopyrus kaki, Hibiscus rosasinensis*, have shown potential for the synthesis of nanoparticles is yet to be fully explored[14-17].

Here we have used the leaf extract of *Solanum virginianum* to synthesize silver nanoparticles. These prove to be both as reducing agent and capping agent. *Solanum virginianum (family: solanaceae)* is an important medicinal weed in traditional ayurvedic health care systems. The root extract is used to cure urinary diseases, cough and hair fall. Leaf extract is useful in thetreatment of fever, cough, Asthma, Sore throat, Rheumatism and treated for gonorrhea, influenza and enteric fever[18]. Optimization of process parameters helps the production of high-qualitynanoparticles minimizing the variable interventions. Response surface methodology is one such tool to used various design experiments which render in less time consuming rather than usual laborious trials. The application of central composite design (CCD) is useful to study the interactions among variables and optimize the experimental conditions based on second order polynomial equation. Furthermore, these designs enhance the process settings against other influencing factors[19,20]. In this work, CCD used for optimization of process parameters like reaction time, temperature, pH and concentration of plant extract which affects the bioreduction of silver nitrate. Furthermore, the application of ANN modeling has also been used to validate the experimental data.

MATERIALS AND METHODS

Plant material and synthesis of silver nanoparticles

*Solanum virginianum*leaves from the local orchard were taken adjacent the institute at Chennai, Tamilnadu, India. The leaves were washed, dried and prepared as anextract by boiling and filtering it. 0.01M silver nitrate supplemented to extract from the leaves to scale up the volume up to 25 ml and heated at various temperatures, pH condition.A variation in color was perceived during the heating process.

Spectra investigation

The reduction of silver (Ag) ions from the absorption (UV-Vis) spectrum of the reaction mixture atvarious wavelength to ensure the maximum absorbance (as shown in Fig.1) through spectrophotometer.

Standard Graph:

The standard graph resulted by varying the nanoparticles concentration (3000-15000 µg/ml) in millipore water. The graph measured as thevolume of silver nanoparticle versus OD absorbance at 425 nm.

Response surface optimization

RSM involved in the optimization of various parameters for silver nanoparticle synthesis by bioreduction method. CCD obtained the statistical method with four independent variables (pH, reaction time, temperature, theconcentration of plant extract). Fractional factorial CCD generated 31 experiments based on three factors for five different levels. Upon completion of the experiments, the OD ofnanoparticleproduction used as the output.The polynomial model obtained by regression techniques for four factors using MINITAB 17 determines the optimal response region of the silver nanoparticles yield from bioreduction of silver nitrate. Where Z is the output, X_1-$_4$ are the input λ,l0 is the regression constant , I_1-$_4$ the linear effects, $I_1^{1\text{-}44}$ the squared effects and $I_{12'13,\ 14'\ 23'24'\ 34}$ are interaction terms.

$$Z=\lambda_0+\lambda_1X_1+\lambda_2X_3+\lambda_3X_3+\lambda_4X_4+\lambda_{11}X_1+\lambda_{22}X_2^2+\lambda_{33}X_3^2+\lambda_{44}X_4^2+\lambda_{12}X_1X_2+\lambda_{14}X_1X_3+\lambda_{14}X_1X_4+\lambda_{23}X_2X_3+\lambda_{24}X_2X_4+\lambda_{34}X_3X_4 \quad (1)$$

ANN modelling

The input of ANN is weighted, and thesum of the weighted inputs along with bias values will help to support the input values to next function (Vedaraman *et al.* 2017). This function will be able to determine the input/output behavior that also contributes to nonlinear modeling and stability of neural network involved in the process. These input values processed with neuron and the output will be developed based on the propagation model. In this study, a commonly used forward feed propagation model (Fig. 1.) was used to predict the concentration of silver nanoparticles. In the neural network, each neuron is embedded to another set of aneuron through adaptable weight. Levenberg Marquardt, thegradient descendent method was adopted as amodel training and learning function.

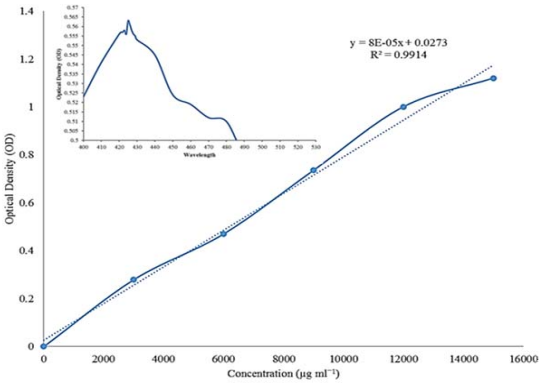


Fig.1. UV–vis absorption spectra of synthesized AgNPs

RESULTS AND DISCUSSION

UV-Vis spectra analysis and Standard graph:

A color change of reaction mixture because ofthe ionic reductioninto Ag particles owing to surface plasmon resonancewith plant extract. The result found paves the way for identifying potential weeds for synthesizing Ag nanoparticles. The standard graph shown in Fig.1. was prepared by varying the nanoparticles concentration (3000-15000µg ml^{-1}) in millipore water at 425 nm. The absorbance values plottedagainst concentration to obtain regression equation.

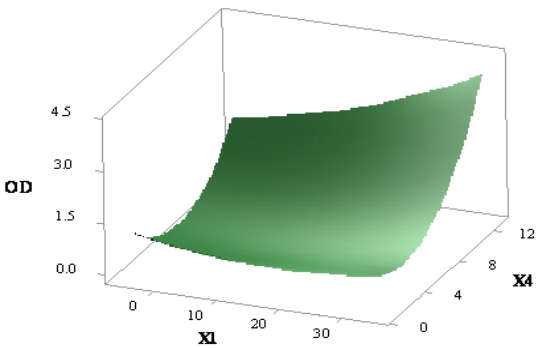
$$Z = 0.2029 - 0.2529X_1 - 0.1540X_2 + 0.0426X_3 - 0.4658X_4 + 0.0912X_1^2 + 0.0678X_2^2 - 0.0035X_3^3 + 0.3314X_4^4 - 0.0997X_1{}^*X_2 + 0.0253X_1X_3{}^* + 0.1557X_1{}^*C_4 + 0.0024X_2{}^*X_3 + 0.1346X_2{}^*X_4 - 0.0222C_3{}^*X_4$$

Optimization of silver nanoparticle production by RSM method:

Second order polynomial equation is used in CCD to generate the predicted data based on the input and variables (Table 1). Moreover, the surface plots under CCD helps to exemplify input based on single and interactive effects of the response. Also, the second order regression equation post-ANOVA analysis yields the quantity of Ag-NPs synthesizedon assigned input of the variables (Table 2 & Table 3). Based on the coefficients of ANOVA the equation was fitted accordingly and are shown below.

The response model shows that experimental data and predicted output are very linear with R^2>0.9 (Table 1) close to unity indicating model can elucidate 96% response variability. Furthermore, the linear and quadratic terms based on the model (Table 2) were significant for plant extract, temperatureure, time and pH ($p<0.05$).

The response surface plots relating combined effects among variables for silver nanoparticles synthesis depicted in Fig. 2. resulting from two variables constant at their middle level. Fig. 2a shows the interaction outcome of plant extract (X1), pH (X4) on nano particle's yield. It was observed that at initial levels of pH, the synthesis of nanoparticles was very low even there is an increase in plant extract concentration. Although, when the pH increases along with higher extract showed a good increase in the AgNPs synthesis. This may be because higher pH supported the stability of nanoparticles. These results were consistent with the literature (Singh *et al.,* 2009; Iravani *et al.,* 2014).The effect of temperature (X2) and plant extract (X1) on the AgNPs synthesis is shown in Fig. 2b. It can be noted that lower levels of plant extract reflected in higher absorbance with anincrease in temperature. However, ahigher concentration of AgNPs observed at lower temperature levels with anincrease in plant extract concentration. This may attribute to the increase in response proportions owing to temperature deviations, and the result is inconsistent with literature (Jiang *et al.,* 2011).However, Sun *et al* 2014, in his study observed that effect of



(a)

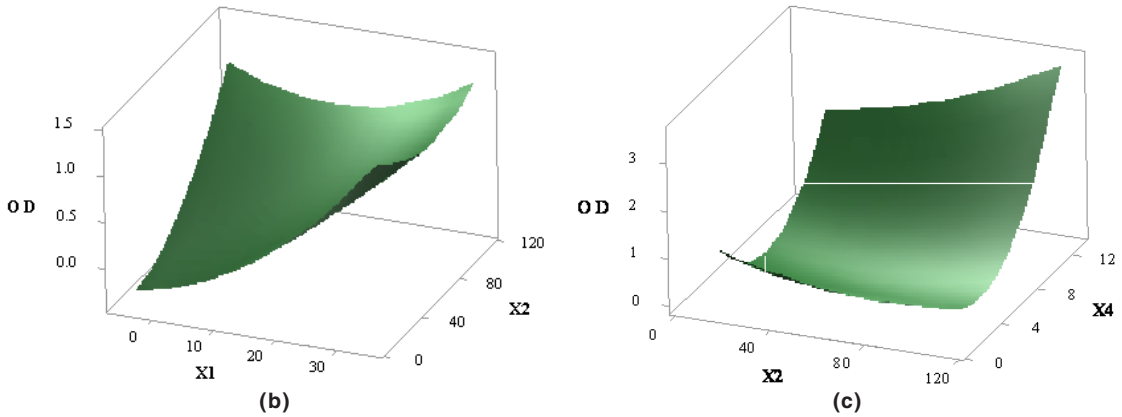


Fig. 2. Response surface plots A) Plant extract (X1) vs pH (X4); B) Plant extract (X1) vs Temperature (X2); C) Temperature (X2) vs pH (X4

Table. 1: Experimental and predicted results based on CCD & ANN

Std order	Plant Extract (X_1)	Temperature (X_2)	Time (X_3)	pH (X_4)	Exp. data	Predicted (RSM)	Predicted (ANN)
1	5	40	2	4	0.112	-0.02936	0.37247
2	25	40	2	4	0.196	0.313783	0.22491
3	5	90	2	4	0.148	0.2041	0.45883
4	25	90	2	4	0.317	0.148492	0.22949
5	5	40	20	4	0.164	0.044767	0.32101
6	25	40	20	4	0.226	0.489158	0.055398
7	5	90	20	4	0.201	0.287975	0.57601
8	25	90	20	4	0.519	0.333617	0.35221
9	5	40	2	10	0.16	0.366017	1.5165
10	25	40	2	10	1.419	1.331908	1.3087
11	5	90	2	10	1.401	1.137725	2.22
12	25	90	2	10	1.565	1.704867	0.25509
13	5	40	20	10	0.183	0.351392	1.287
14	25	40	20	10	1.454	1.418533	1.1437
15	5	90	20	10	1.23	1.13285	1.5744
16	25	90	20	10	1.66	1.801242	0.060269
17	-5	65	11	7	0	0.062025	0.97833
18	35	65	11	7	1.1561	1.073558	0.29779
19	15	15	11	7	0.342	0.166158	0.50779
20	15	115	11	7	0.627	0.782325	0.27668
21	15	65	0	7	0.023	0.103492	0.16938
22	15	65	29	7	0.375	0.273992	0.74805
23	15	65	11	1	0.5415	0.596992	2.4568
24	15	65	11	13	2.536	2.459992	0.19032
25	15	65	11	7	0.203	0.202918	0.19032
26	15	65	11	7	0.202429	0.202918	0.19032
27	15	65	11	7	0.203	0.202918	0.19032
28	15	65	11	7	0.203	0.202918	0.19032
29	15	65	11	7	0.203	0.202918	0.19032
30	15	65	11	7	0.203	0.202918	0.19032
31	15	65	11	7	0.203	0.202918	0.19032

Table. 2: Estimated regression coefficient of second order polynomial model

Coefficient	Estimated coefficient	t-value	p-value
λ0	0.2029	3.10	0.007
λ1	0.2529	7.15	0.000
λ2	0.1540	4.36	0.000
λ3	0.0426	1.21	0.245
λ4	0.4658	13.17	0.000
λ11	0.0912	2.82	0.012
λ22	0.0678	2.09	0.053
λ33	-0.0035	-0.11	0.914
λ44	0.3314	10.23	0.000
λ12	-0.0997	-2.30	0.035
λ13	0.0253	0.58	0.567
λ14	0.1557	3.60	0.002
λ23	0.0024	0.06	0.956
λ24	0.1346	3.11	0.007
λ34	-0.0222	-0.51	0.615

temperatures doesn't contribute as the nanoparticles have reached themaximum level of extraction from plant source. The increase in pH with temperature showed a positive effect in the AgNPs synthesis (Figure. 2c).

The application of ANN modeling to the experimental data under Tansig and LM algorithm was used. To develop network, the datawere separatedinto training (70%), validation (15%) and testing (15%) based on Levenberg-Marquardt calculations. From the fig 3a & b after five epoch with the value of 0.09378 and R^2 value close to 1 indicating the goodness of the model. Furthermore, the parameters such pH, temperature and plant extract were significant with $P<0.05$ compared to other interaction factors.

Table. 3: Analysis of variance (ANOVA) for optimization of silver nanoparticles (R^2=96%)

Source	Degrees of freedom	sum of squares	Mean square	F-value	P-value
Regression	14	11.5252	0.82323	27.44	0.000
Linear	4	7.3541	1.83851	61.29	0.000
Square	4	3.3164	0.82910	27.64	0.000
Interaction (Two-way)	6	0.8548	0.14246	4.75	0.006
Residual Error	16	0.4799	0.03000		
Total	30	12.0051			

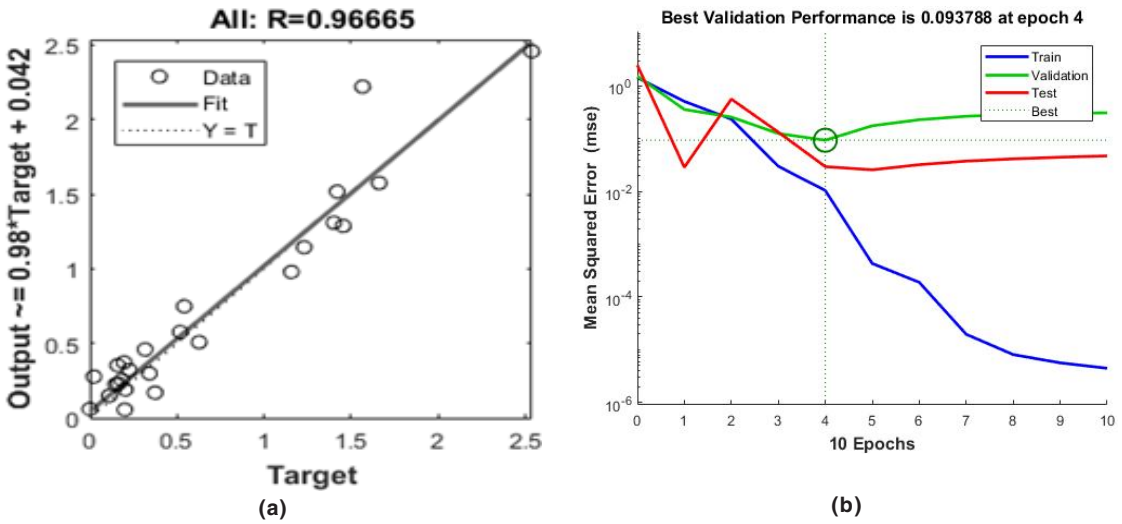


Fig. 3. ANN Simulation A) Regression graph for overall model; B) Performance plot

CONCLUSION

The extraction of AgNPs was extracted using chemical mediated methods based on central composite design. It was observed that higher pH supported the increased extraction of AgNPs from the solution. This was significant with other two parameters such as temperature and plant extract with $p<0.005$.Both the model viz., RSM & ANN showed regression coefficient of 0.96 which is very close to 1 indicating the data's are statistically significant. This study demonstrates that plant extract would be viable source for nanoparticles synthesis compared to other sources which is of many significant applications.

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