

Optimization of green synthesis of ZnO nanoparticles by *Dittrichia graveolens* (L.) aqueous extract

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ABSTRACT

In this work, we reported synthesis of ZnO nanoparticles (ZnONPs) by green procedure. A simple and effective synthesis of ZnONPs was performed by *Dittrichia graveolens* aqueous extract. The effect of three parameters including pH of the Zinc solution (4.0, 6.0 and 8.0), time (40, 60 and 120 min) and extract ratio (25 and 75 %) were studied and optimized using Response Surface Methodology (RSM). The ZnONPs were characterized by UV-Vis, FTIR and FESEM methods. The size of particles were around 100 nm. This new eco-friendly synthesis of ZnONPs is a convenient technique for large scale commercial manufacture of ZnONPs.

Keywords: Green Synthesis; *Dittrichia graveolens* (L.); Response Surface Methodology (RSM); Zinc Oxide Nanoparticles; UV-Vis; FESEM

INTRODUCTION

Newly, many improvements in the field of nanoparticle synthesis from different materials and strict control on their size, composition and

uniformity have been accomplished [1]. Nano materials can show atom like behaviors which obtained from premier surface energy due to their wide surface area and larger band gap between

valence and transition bands when they are divided to atomic size [2]. Zinc oxide (ZnO) is stable in chemical process, Non-toxic, biocompatible, low cost, and eco-friendly [3]. ZnO, an agent of II–VI semiconductor compounds group, has attracted significant consideration over the last few years. Many attractive properties, such as the direct wide band gap (3.37 eV), large excited binding energy (60 meV at room temperature), good piezoelectric characteristic, chemical stability and biocompatibility could be suggested a host of practical usage, special in the area of ultraviolet emission device [4]. Furthermore, ZnONPs have special physiognomy like high electron mobility, tunable band position, high catalytic activity, excellent photo sensitivity, high chemical and thermal stability, non-toxicity and cost effectiveness [5]. It has been extensively studied for a diversity of applications in optical coatings, solid-state solar window layers, electro optic modulators, photoconductors, field effect transistors, optical sensors, photo catalysts, electroluminescent materials, phosphors and other light emitting materials. In fact, ZnO has been found special matter in thin film electroluminescent devices, lasers and flat panel displays when doped with divalent manganese ions [6].

Many physical and chemical procedures have been used for the synthesis of great amount of metal nanoparticles in comparatively short

period of time, such as solution based methods, chemical precipitation, sol–gel, solvothermal/hydrothermal, electrochemical and photochemical reduction techniques [2]. However, physical and chemical methods are rampant in nanoparticles synthesis, the green synthesis is the best sanitation method due to the conservation of the environment as well as the synthesized small nanoparticles with and large surface area. The plant phytochemicals with antioxidant properties are accountable for the synthesis of metal and metal oxide nanoparticles. This useful reaction is rapid, readily conducted at room temperature and pressure and easily scaled up. Laterally, synthesis of nanoparticles has been done by bacteria, fungi, actinomycetes. Moreover, the use of the extract of *Azadirachta indica*, *Camellia sinensis*, *Corriandrum sativum*, *Nelumbo nucifera*, *Ocimum sanctum* and many other plants by green chemistry that is friendly environment [7]. The green synthesis avoids using of toxic chemicals and excessive temperature and pressure conditions against formal chemical and physical methods [8].

In this work, ZnO nanoparticles were prepared by an aqueous leaf extract of *Dittrichia graveolens*, optimized and evaluated using Response surface methodology (RSM).

MATERIALS AND METHODS

Zinc nitrate was purchased from Aldrich. Ethanol was purchased from Hamoun Teb Markazy. *Dittrichia graveolens* were collected from Gorgan (Golestan, Iran); it was then washed three times with distilled water and dried in the shade.

Green synthesis of ZnONPs

8 g of *Dittrichia graveolens* powder was placed in a flask containing 200 ml of distilled water and then boiled for 5 min. The mixture was cooled and centrifuged at 3500 rpm for 10 min. The clear supernatant was stored at 4 °C. To synthesize of ZnONPs, 1mM of zinc nitrate aqueous solution at different pH (4, 6 and 8) were mixed with several ratios of leaf extract (75:25 and 25:75) in various time (40, 80 and 120 min) and stirred at room temperature. The precipitate was collected by centrifugation, washed with deionized water and ethanol for several times, and suspended in 7 ml of distilled water. Four examinations were performed to study the effect of pH, metal to extract ratio (v/v) and time (Table 1). The formation of ZnONPs were monitored by r UV–Vis spectra.

Statistical analysis

Response Surface Methodology (RSM) is one of the useful statistical and mathematical methods which we can explain the relationship between the response and independent variables.

Software of RSM defines the effects of independent variables in the processes. In order to analyze the effects of independent variables, this experimental methodology (RSM) provides a mathematical model. In this research, the main and mutual effects of the factors obtained, so that the statistical design of the response surface was chosen [9]. Model being used in the RSM is usually a quadratic relationship. In the RSM, for each dependent variables, one related model is defined which states the main and mutual effects of the factors for each variable alone. In this research, three variables including the time (40, 60 and 120 min), plant extract ratio (25 and 75 %) and pH (4, 6 and 8) were used to study ZnONPs synthesis yield and also to optimize the mentioned process. The software of Design Expert 10 was used to obtain the experimental projecting and RSM data to analyze the results.

Characterization of ZnONPs

8 g of powdered curcumin was placed in the flask containing 200 ml of ethanol and then boiled for 5 min. The mixture was cooled and centrifuged at 3500 rpm for 10 min. The clear supernatant was stored at 4 °C. 25 ml of zinc nitrate solution (pH 4) was mixed with 75 ml of plant extract (extract ratio 75 %) for 40 min and stirred at room temperature, then 10 ml of turmeric plant extract was used to synthesize bioactive curcumin and this curcumin extract

was used as a stabilizer for zinc nanoparticles [10]. 20 ml of solution was centrifuged and the precipitation was collected and washed with deionized water and ethanol several times, and analyzed using UV-Vis technique.

RESULTS AND DISCUSSION

UV-Vis analysis

The UV-Vis absorption spectrum increases with increasing of NPs related concentrations. The absorption spectra of the synthesized samples are shown in Fig. 1. All the samples show two sharp characteristic absorption peak at 285 and 320 nm which is due to the intrinsic band gap absorption of ZnO. The absorbance peak at 285 showed the absorption spectra of the ZnO solutions with various impurities [11]. The ZnO had strong absorbance at the related wavelength (310–385 nm) [11]. The absorbance peak of the

ZnO is observed at 320 nm. The absorbance peaks at 285 nm were reported at Table 1.

Fig. 1. UV-Vis spectrum of synthesized ZnONPs

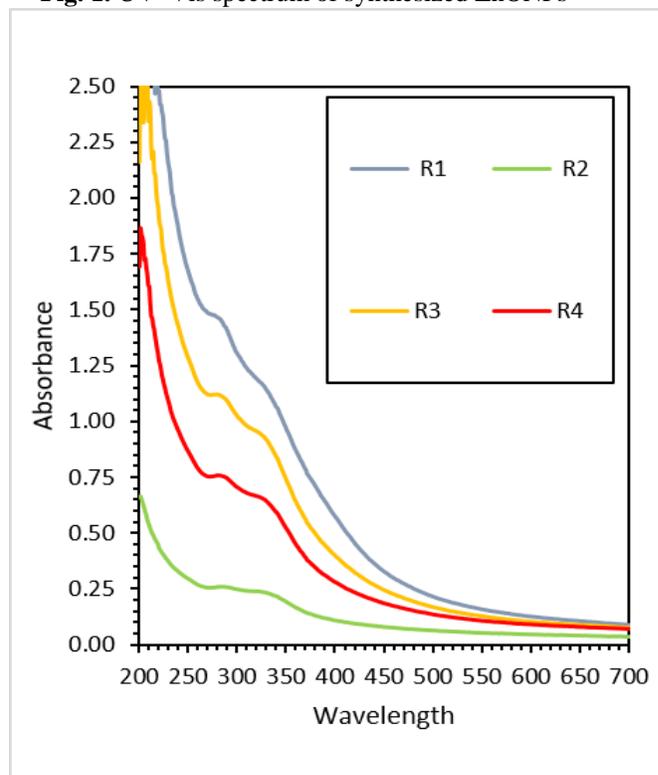


Table 1. Experimental planning

Run	A:Extract %	B:pH	C:time min	Absorbance
1	75	4	40	1.4413
2	25	4	120	0.2596
3	75	6	80	1.1113
4	75	8	120	0.7635

Optimization of green synthesis by response surface methodology (RSM)

The analysis of variance (ANOVA) are shown in Table 2 and the values of coefficients are

reported in Table 3. The coefficient of determination (R^2) of the model is 0.9999 (Table 4), which showed that the model is proper to much display the real communication between

the parameters chosen. The final obtained equation is shown in equation 1.

$$\text{Absorbance} = 0.51 + 0.59A - 0.34B + 0.000C \quad (1)$$

A= Extract
B= pH
C= time

Table 2. Analysis of variance

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	0.77	2	0.38	7254.74	0.0083
A-Extract	0.77	1	0.77	14496.47	0.0053
B-pH	0.23	1	0.23	4349.95	0.0097
C-time	0.000	0			
Residual	5.281E-005	1	5.281E-005		
Total	0.77	3			

Table 3. Values of coefficients

Factor	Coefficient Estimate	df	Standard Error	% CI Low	95% CI High	VIF
Intercept	0.51	1	4.920E-003	0.45	0.58	
Extract	0.59	1	4.920E-003	0.53	0.65	1.38
pH	-0.34	1	5.138E-003	-0.40	-0.27	1.38
time	= C + Intercept - A + B					

Table 4. R-Squared of model

SD	7.267E-003	R-Squared	0.9999
Mean	0.89	Adj R-Squared	0.9998
C.V. %	0.81	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	188.244
-2 Log Likelihood	-33.59	BIC	-29.43
		AICc	

In Fig. 2 the response surface plot obtained as extract ratio against pH for incubation period of 80 min. A linear increasing in absorbance with increasing in extract ratio and decreasing in pH

was observed. The plot indicating that absorbance is good in acidic solution (pH 4).

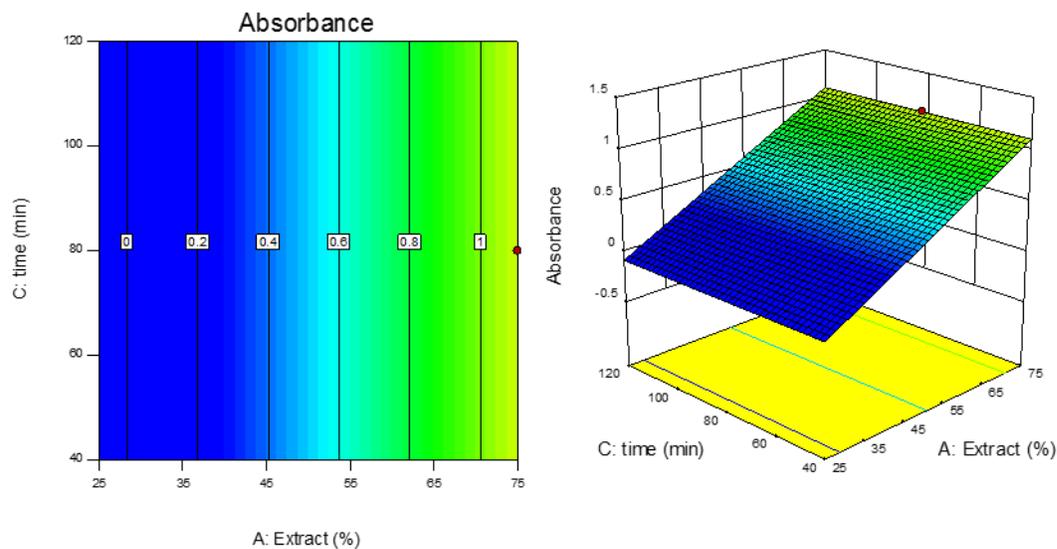


Fig. 2. Response surface plot showing the effect of extract ratio (%), pH and their mutual interaction on the absorbance.

In Fig. 3 shows the effect of time and extract ratio on the absorbance. Since time has any effect on the absorbance amount, further increasing in time

has no effect on the absorbance. As the extract ratio increases, the absorbance was higher.

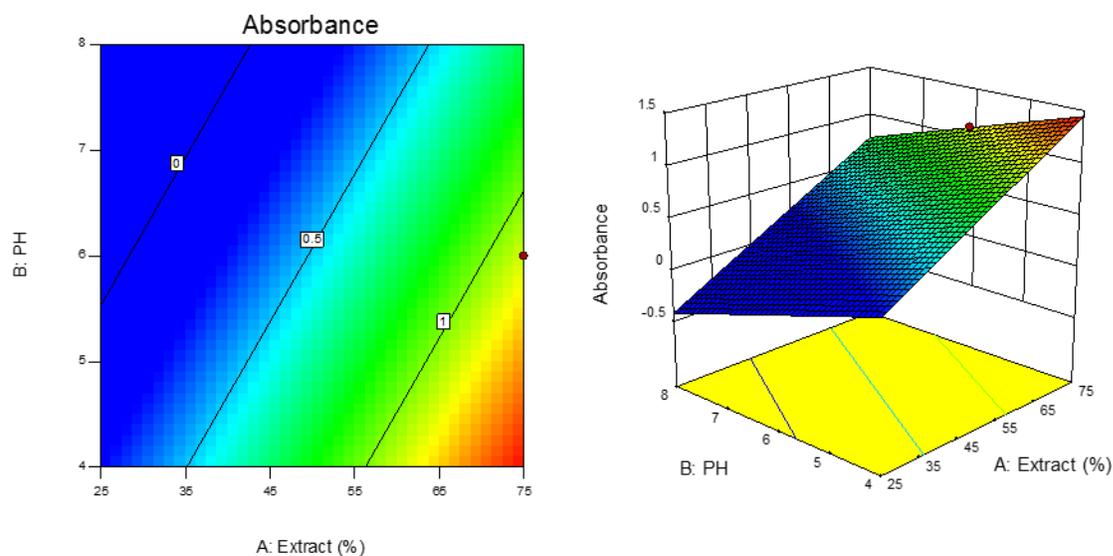


Fig. 3. Response surface plot showing the effect of extract ratio (%), time and their mutual interaction on the absorbance.

The effects of time and pH are shown in Fig. 4 for the absorbance at extract ratio 50 %. A linear

increasing in absorbance with decreasing in pH has been observed.

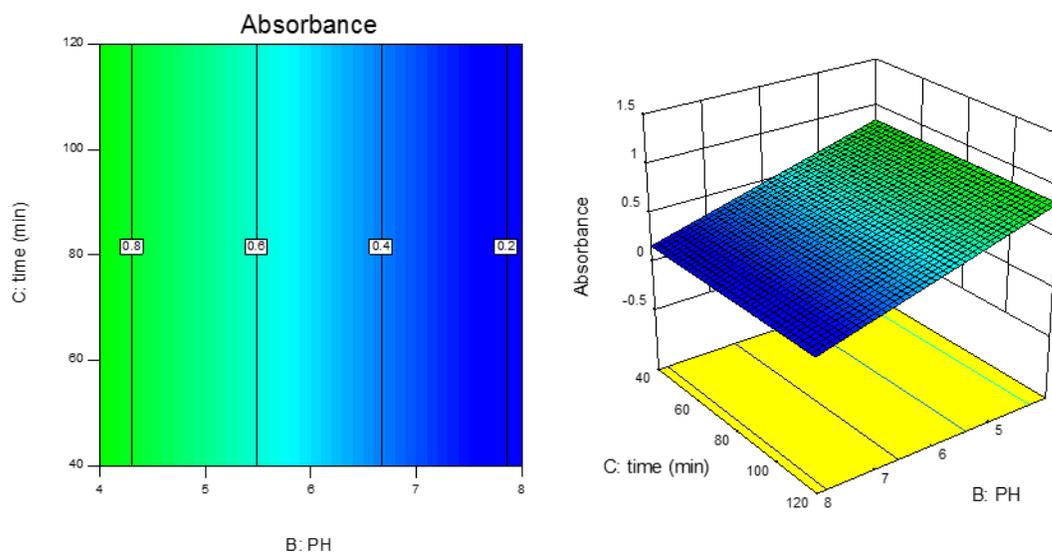


Fig. 4. Response surface plot showing the effect of pH, time and their mutual interaction on the absorbance.

Effect of each factor has shown in Fig. 5. The results show that the maximum effective factors were extract ratios and the plots show that

increasing the extract ratios, increase the synthesis of nanoparticles.

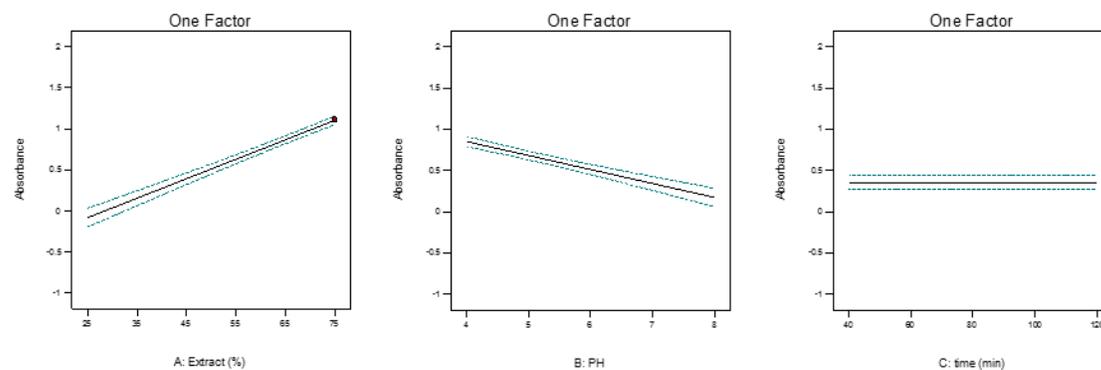


Fig. 5. Effect of factors on absorbance

Characterization of ZnONPs

UV-Vis spectroscopy

In the second experiment using curcuma extract from turmeric as a stabilizing agent for prevent the accumulation of ZnONPs [10]. Interestingly, two sharp absorption peaks located at 235 and 323 nm are observed in Fig. 6, which are specified to the absorption of $Zn(OH)_2$ and ZnO, respectively [12]. The absorption peaks were previously observed for the layered $Zn(OH)_2$ [12]. The researchers have observed that the ZnO had strong absorbance at the related wavelength (310–385 nm) [11]. Optical characterizations such as UV-Vis absorption is sensitive to the surface, so surface information's can be obtained [12].

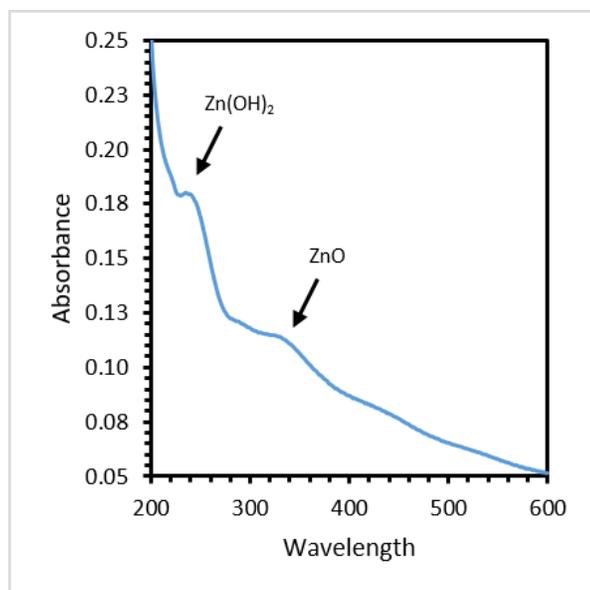


Fig. 6. UV-Vis spectrum of synthesized ZnONPs

FTIR spectroscopy of ZnONPs

FTIR analysis of ZnONPs was performed in the wave number range from 400 to 4000 cm^{-1} using the KBr as shown in Fig. 7. The wide absorption peak at 3500 cm^{-1} shows the stretching vibration of the O-H group. The absorption peaks at 2300 and 2400 cm^{-1} are assigned to the CO_2 group [13]. The absorption peaks at 1656 and 1427 cm^{-1} are assigned to C=C stretching and C-C stretching vibrations, respectively [14].

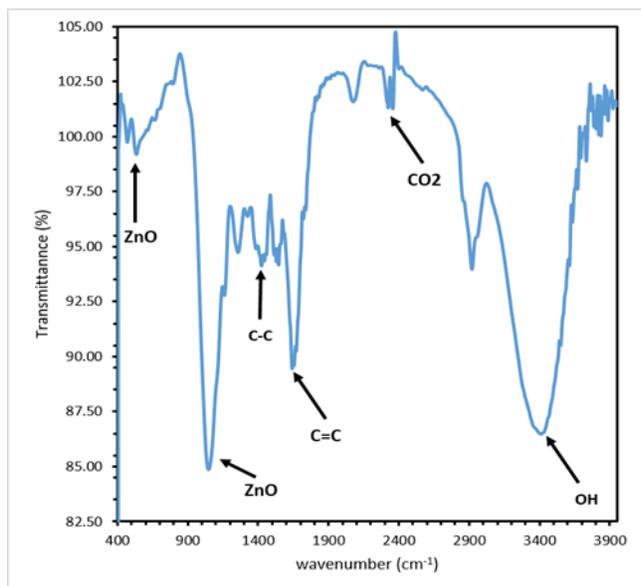


Fig. 7. FTIR spectrum of ZnO nanoparticles

FESEM analysis of ZnONPs

FESEM images were carried out based upon the surface study. The FESEM studies prepare the information on the morphology, particle size, and perspective ratio. Synthesized ZnONPs were

spherical in shape [15]. The FESEM micrographs in Fig. 8 shows well dispersed, versatile and spherical shape dispensation of ZnONPs prepared with *Dittrichia Graveolens* extract with particle sizes about 100 nm [16].

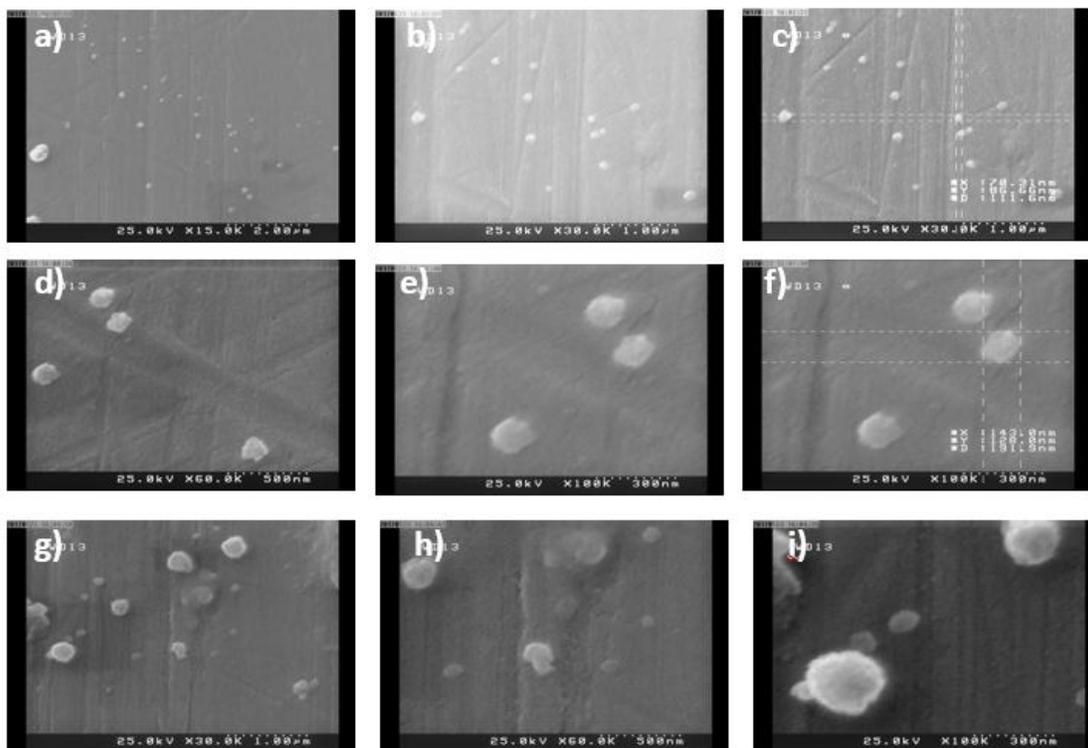


Fig. 8. FESEM images of prepared ZnONPs

CONCLUSION

Synthesized ZnONPs using *Dittrichia graveolens* (L.) extract is green, fast and economical synthesis. This work was performed to optimize the synthesis of ZnONPs using Response Surface Methodology (RSM). ZnONPs have been successfully synthesized and optimized using *Dittrichia graveolens* extract as reducing agent and *Turmeric* extract as stabilizing agent. UV-Vis, FTIR and FESEM

studies were performed to analyze the ZnONPs. FESEM analysis demonstrated presence of the spherical nanoparticles with size about 100 nm. The synthesis carried out using plant extract by a simple reaction at room temperature without any catalysts. The ZnONPs synthesized by green method displayed degradation ability of *Dittrichia graveolens*. Thus, this study will be useful for easy, low cost, and eco-friendly manufacturing of ZnONPs.

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