# *Gomphrena serrata* Leaf Extract as Corrosion Inhibitor and Reductant for the Synthesis of Copper Nanoparticles

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Adapting eco-friendly methodologies is the need of the hour in the every field of research. In the present work an investigation on *Gomphrena serrata* leaves was evaluated as a corrosion inhibitor for the mild steel in HCl medium and as a reductant. The *G. serrata* as an efficient inhibitor it obeys Langmuir adsorption isotherm and served as anodic type inhibitor. The impedance study confirms the formation of thin film on the metal surface through its $C_{dl}$ and $R_{ct}$ values. The copper nanoparticles and their derivatives have been used as a medicine to prevent infection, leg ulcers *etc*. *Gomphrena serrata* leaves have good medicinal values, to enhance its medicinal properties it was mediated for the synthesis of copper nanoparticles. The CuNPs formation was confirmed by SPR bands at 345 nm by microwave method and at 341 nm by thermostat method. The functional groups present in the *G. serrata* also present in the FTIR spectra of CuNPs and it confirms the *G. serrata* was used as a reducing as well as a capping agent.

**Keywords:** *G. serrata*, Corrosion inhibitor, CuNPs.

## INTRODUCTION

*Gomphrena serrata* leaves belongs to the Amaranthaceae family and recognized as medicine for bronchial asthma, diarrhea, hay fever, pains, tonic, carminative, diabetes, dermatitis and piles [1,2]. Plants are the gracious gift, as it has various attributes towards the human life and the phyto constituents present may be the responsible for the healing property. Based on the attributes and to adopt the green principle of "Source Reduction–substitution of raw materials" the plants are accepted as green inhibitors and green reducing agents. Mild steel is a significant metal, which has diverse application in industries and its deterioration causes a major economic loss. Using corrosion inhibitors the deterioration can be prevented and protected [3-5]. Though the synthetic organic inhibitors show high inhibitive effect towards the corrosion, it affects the environment during its process [6]. Green inhibitors are accepted by the researchers as they are ecologically acceptable, environmental friendly, low-cost and non-toxic [7-9]. Copper nanoparticles has significant role in the medicinal field such as wound dressings and biocidal effects [10]. The nanoparticles have a greater surface area per weight than larger particles,

which causes them to be more reactive and enhance the therapeutic effectiveness to targeted drug delivery. Here the present work was to investigate the *Gomphrena serrata* leaves as a corrosion inhibitor for the mild steel in 0.5 M HCl medium and as a reducing and a capping agent for the synthesis of copper nanoparticles.

## EXPERIMENTAL

**Preparation and phytochemical analysis of leaf extract:** Fresh leaves of *G. serrata* were collected from in and around Tiruchirappalli. The fresh leaves were dried under shade and extraction of the crude sample was carried out using cold percolation method [11]. The active phyto compounds present in the leaf extract was analyzed using preliminary phytochemical standard procedures [12].

**Determination of corrosion rate by weight loss measurements:** The mild steel coupons (0.026 % S, 0.06 % P, 0.4 % Mn and 0.1 % C and rest Fe) were immersed in beaker containing 100 mL acid solution without and with different concentrations of *G. serrata* leaves extract using hooks. The tested specimen was cleaned and weighed under ASTM G-81 procedure. By varying the concentration, time and temperature

the studies were carry out and the % inhibition efficiency and the corrosion rate was calculated using the formulae:

$$\text{Corrosion rate (mpy)} = \frac{87.6 \times W}{A \times T \times D} \quad (1)$$

**Electrochemical measurements:** The charge transfer resistance ($R_{ct}$) and capacitance double layer ($C_{dl}$) were calculated using AC signals of amplitude 10 mV peak-to-peaks at the open circuit potential in the frequency range of 10 MHz to 1 Hz through electrochemical impedance spectroscopy using Electrochemical System Model Vertex 100 mA.D with IVIUM software. The $I_{corr}$ and $E_{corr}$ values were calculated using potentiodynamic polarization with scan rate of 5 mV s$^{-1}$. The polarization resistance ($R_p$) was calculated from the linear polarization measurement.

**Morphological investigation:** The surface morphology of the mild steel specimen immersed in the presence and absence of the *G. serrata* were studied by FTIR using Perkin-Elmer 1600 FTIR spectrophotometer with a resolving power of 4 cm$^{-1}$ and SEM using F E I Quanta FEG 200-High resolution scanning electron microscope (SRM University, Kattankulathur).

**Green synthesis of copper nanoparticles:** The pilot experiments were carried out using 1 mL of 1 mM copper sulphate with 1 mL of *G. serrata* extract and kept in a microwave oven and duplicate is kept in thermostat at room temperature for 1 h. The change in colour confirms the presence of copper nanoparticles.

**Characterization of copper nanoparticles:** The synthesized copper nanoparticles was monitored by SPR band of UV-visible spectroscopy and the active biomolecules present in the *G. serrata* were responsible for the stabilization of copper nanoparticles was confimed by FTIR studies.

## RESULTS AND DISCUSSION

The presence of alkaloid, tannin, flavonoid, proteins, steroids, carbohydrates, poly phenol, glycoside, terpenoids and triterpenoids were confirmed by the preliminary qualitative analysis. These active biomolecules are responsible for the special properties.

**Weight loss measurements:** The weight loss method reveals that the corrosion rate decreases and the inhibition efficiency increases with increasing *G. serrata* concentration. The corrosion rate decreases due to the adsorption and coverage of the inhibitor molecule on the metal surface. The maximum inhibition efficiency was found to be 86.9 % for 700 ppm (Fig. 1). As the corrosion rate is temperature dependent the studies show that the corrosion rate increases with increasing the temperature because of the desorption of molecules from the metal surface (Table-1).
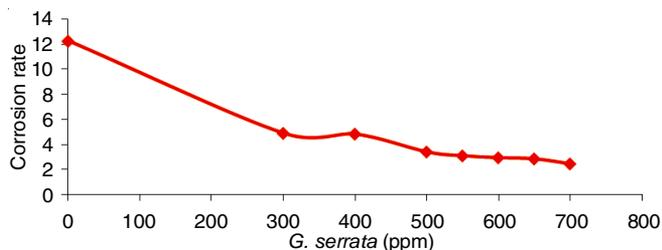


Fig. 1. Corrosion rate of *G. serrata* at different concentration

| TABLE-1 |
|---|
| EFFECT OF TEMPERATURE ON THE CORROSION RATE OF *G. serrata* AT 700 ppm |

| Temp. (K) | Corrosion rate | | IE (%) |
|---|---|---|---|
| | Blank | *G. serrata* | |
| 303 | 12.2334 | 2.6700 | 86.90 |
| 313 | 21.4000 | 6.1000 | 76.80 |
| 323 | 31.7200 | 15.2999 | 57.21 |
| 333 | 50.2600 | 36.4200 | 29.62 |

**Thermodyamic parameters:** The temperature dependence of corrosion rate can be evaluated by change in enthalpy ($\Delta H^*$) from transition state equation and energy of activation ($E_a$) from Arrhenius equation [13,14].

From the Arrhenius plot (Fig. 2a) the linear regression of blank and inhibitor are close to unity and the energy of activation is calculated from the graphical method and reveals that the $E_a$ value is higher in the presence of *G. serrata* (83.88 kJ mol$^{-1}$) suggest the formation of thin film on the surface of the metal surface favours the physical adsorption [15]. From the straight line of transition plot slope (Fig. 2b) and the intercept, the enthalpy is calculated. The positive value of $\Delta H^*$ (82.3518 kJ mol$^{-1}$) reflects the endothermic nature which means the metal dissolution is difficult in the presence of *G. serrata* [16].
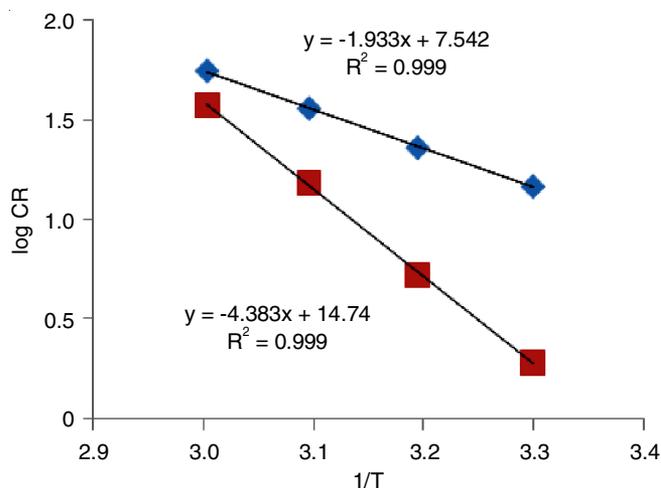


Fig. 2a. Arrhenius plot
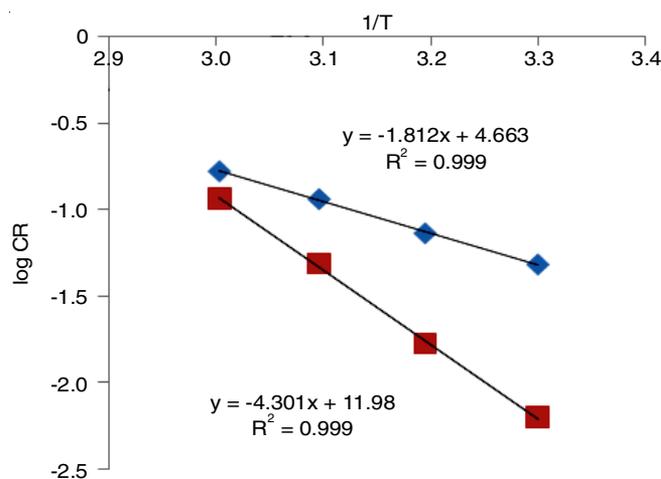


Fig. 2b. Transtition state plot

**Langmuir adsorption isotherm:** This adsorption isotherm gives the information about the interaction of *G. serrata* and the metal surface. The regression value of the straight line is nearly one it indicates the strong adherence of *G. serrata* on the metal surface.

The $\Delta G^{\circ}_{ads}$ is calculated from the eqn. 2 and the $K_{ads}$ values can be calculated from the intercept lines.

$$\Delta G^{\circ} = -RT \ln (55.5\ K_{ads}) \qquad (2)$$

where 55.5 is the water concentration of the solution in mL/L. The calculated $\Delta G^{\circ}_{ads}$ is $-13.717$ kJ mol$^{-1}$ and its negative value implies that the adsorption is spontaneous in nature that means the *G. serrata* bio active molecules are readily adsorbed on the metal surface and retard the surface from corrosion. The calculated $\Delta G^{\circ}_{ads}$ value is $-13.717$ kJ mol$^{-1}$ indicates the electrostatic attraction between the *G. serrata* molecules and the metal surface [17].

**Impedance spectroscopy:** The EIS parameter was calculated from the impedance behaviour of metal surface with and without *G. serrata* and the results are tabulated in Table-2.

**TABLE-2**
**ELECTROCHEMICAL IMPEDANCE PARAMETERS OF *G. serrata***

| System | $R_s$ ($\Omega$) | $R_{ct}$ ($\Omega$ cm$^2$) | $C_{dl}$ (F cm$^{-2}$) |
|---|---|---|---|
| Blank | 23 | 117 | $1.455 \times 10^{-4}$ |
| Inhibitor | 73 | 493 | $1.180 \times 10^{-4}$ |

The $R_{ct}$ value increases from 117 $\Omega$ cm$^2$ (blank) to 493 $\Omega$ cm$^2$ on addition of 700 ppm of inhibitor. The $C_{dl}$ value decreases from $1.455 \times 10^{-4}$ F cm$^{-2}$ (blank) to $1.18 \times 10^{-4}$ F cm$^{-2}$) (Fig. 3). The decrease in the capacitance ($C_{dl}$) on the addition of inhibitor may increase the thickness of the double layer, which increases in local dielectric constant [18].
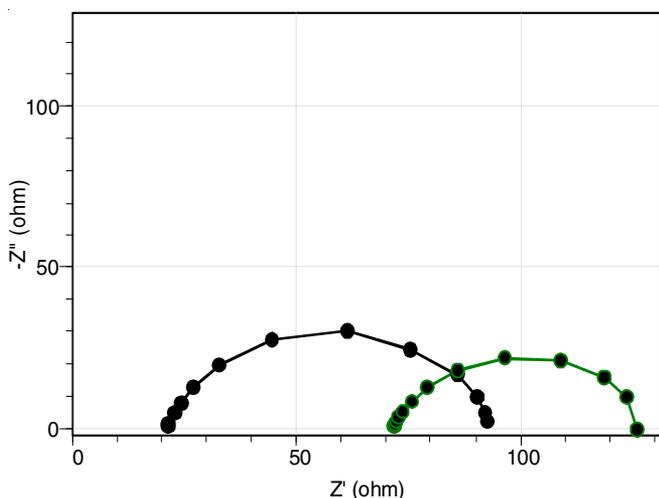


Fig. 3. Nyquist plot in absence and presence of *G. serrata*

**Potentiodynamic polarization:** The potentiodynamic parameters was calculated from the potentiodynamic polarization curves which shows on the addition of *G. serrata* decreases the corrosion current density ($I_{corr}$). The addition of *G. serrata* shift the $E_{corr}$ value, which suggest the reaction is anodic controlled. Anyhow the maximum shift is only 32 mV, which may behave as a mixed type inhibitor (Table-3). The addition of *G. serrata* reduces the anodic dissolution of metal and retards the cathodic evolution reaction (Fig. 4).
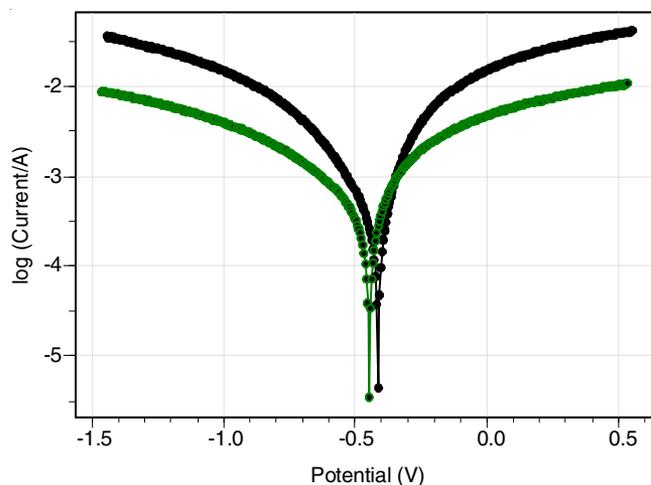


Fig. 4. Tafel polarization curves of *G. serrata*

**Morphological investigation**

**SEM analysis:** The surface analysis of the specimen establish the interaction of inhibitor molecules with metal surface. SEM images (Fig. 5) revealed that mild steel specimen dipped in 0.5 M HCl for 3 h have lot of pits and cavities and the specimen in presence of *G. serrata* have smoothened surface, where the active phytochemicals are adsorbed on the metal specimen which retards the corrosion rate [19].

**FTIR analysis:** The FTIR spectra have been used to analyze the protective film formed on the metal surface. The FTIR spectrum of *G. serrata* shows a band at 3469.58 and 3431.41 cm$^{-1}$ may be phenolic –OH stretching frequency and –NH stretching frequency respectively. The band at 1633.61 cm$^{-1}$ is due to C=O stretching and the bands at 1357.20 cm$^{-1}$ is due to O–H in plane bending vibrations, while the band at 671.11 cm$^{-1}$ is due to the presence of aromatic ring [20]. The FTIR spectrum of the thin film formed on the surface of the mild steel after immersing the coupon in 0.5 M HCl containing 700 ppm of *G. serrata* extract for 3 h. The band appears at 3414.88 cm$^{-1}$ due to –OH stretching, the band at 2830.98 cm$^{-1}$ due to –CH stretching of methoxy group and the band appear at 1633.61 cm$^{-1}$ in *G. serrata* is shifted to 1593.27 cm$^{-1}$ and the new peaks appear at 1714.56 cm$^{-1}$ (C=O), 1363.51 cm$^{-1}$ (C–N) and 1222.97 cm$^{-1}$ (C–O) are due to amide stretching frequencies [21].

Based on the above characterizations the *G. serrata* was proved to be an efficient inhibitor and this was further confirmed by comparing the *G. serrata* with other inhibitors and tabulated in Table-4.

**TABLE-3**
**POTENTIODYNAMIC POLARIZATION AND LINEAR POLARIZATION PARAMETERS OF *G. serrata***

| System | $E_{corr}$ (mV/SCE) | $I_{corr}$ ($\mu$A cm$^{-2}$) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $R_p$ |
|---|---|---|---|---|---|
| Blank | -416.4 | 369 | 943 | 750 | 110.1 |
| Inhibitor | -448.0 | 161 | 1139 | 930 | 134.0 |
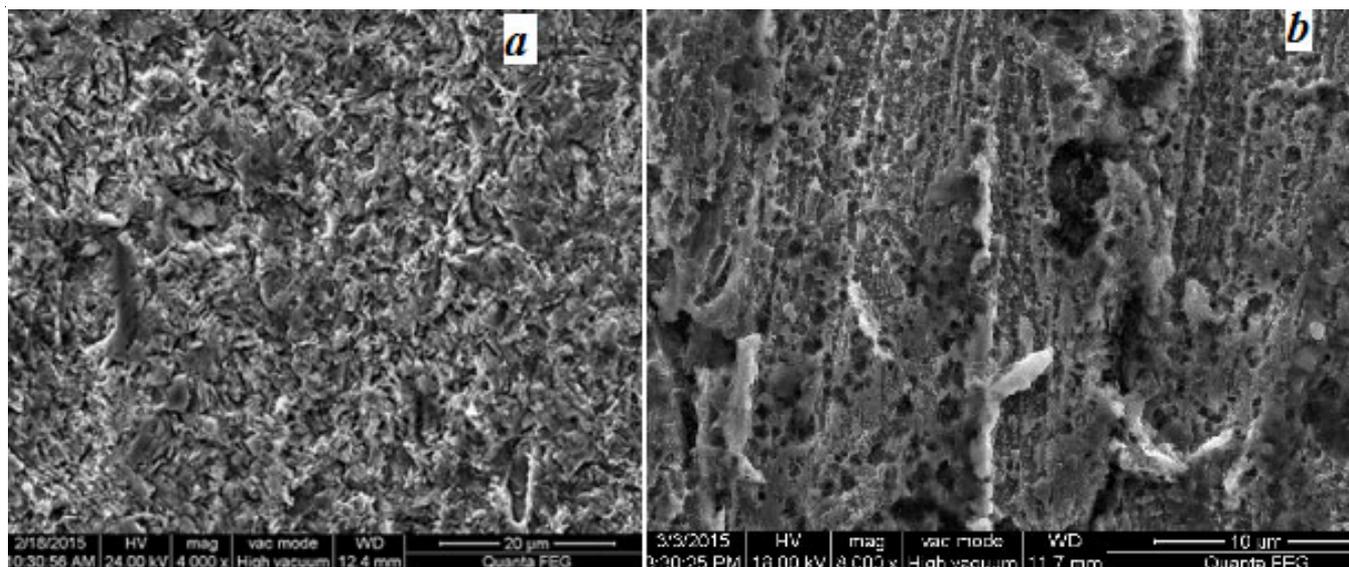
Fig. 5. SEM micrograph of (a) mild steel immersed in 0.5 M HCl (b) mild steel immersed in the presence of *G. serrata* in 0.5M HCl

TABLE-4
CORROSION CURRENT DENSITY ($I_{corr}$) AND CHARGE TRANSFER RESISTANCE ($R_{ct}$) OF *G. serrata*
IN 0.5 M HCl MEDIUM FOR MILD STEEL IS COMPARED WITH OTHER EXTRACTS

| Plant extract | Concentration | Corrosion current density ($I_{corr}$, A cm$^{-2}$) | Charge transfer resistance ($R_{ct}$, Ω cm$^2$) | Ref. |
|---|---|---|---|---|
| *Gomphrena serrata* leaves | 700 ppm | $161.0 \times 10^{-6}$ | 493.0 | This work |
| *Cissus quadrangularis* leaves | 200 ppm | $2.768 \times 10^{-4}$ | 56.0 | [22] |
| *Ziziphus mauritiana* leaves | 2800 ppm | $0.613 \times 10^{-3}$ | 163.3 | [23] |
| *Lycium shawii* | 0.01 g/100 mL | $0.680 \times 10^{-3}$ | 73.6 | [24] |
| *Teucrium oliverianum* | 0.01 g/100 mL | $1.230 \times 10^{-3}$ | 73.6 | [24] |
| *Ochradenus baccatus* | 0.01 g/100 mL | $0.710 \times 10^{-3}$ | 112.7 | [24] |
| *Anvillea garcinii* | 0.01 g/100 mL | $1.280 \times 10^{-3}$ | 66.6 | [24] |
| *Cassia italic* | 0.01 g/100 mL | $1.770 \times 10^{-3}$ | 23.6 | [24] |
| *Artemisia sieberi* | 0.01 g/100 mL | $0.420 \times 10^{-3}$ | 62.3 | [24] |
| *Carthamus tinctorius* | 0.01 g/100 mL | $0.510 \times 10^{-3}$ | 46.1 | [24] |
| *Tripleurospermum auriculatum* | 0.01 g/100 mL | $1.420 \times 10^{-3}$ | 62.0 | [24] |

**Synthesis of copper nanoparticles using *G. serrata***

**Visual observation:** The visual observation of sea green colour confirms the formation of *G. serrata* mediated copper nanoparticles. Initially the extract was yellow in colour, after 1 h at room temperature and 5 min in microwave method the colour formation confirms the formation of copper nanoparticles [25].

**Effect of thermostat and microwave method:** Temperature plays a vital role on the blend of nanoparticles where the *G. serrata* was used as a reductant. The colour changes occurs in 1 mM within 5 min in microwave oven but in thermostat method 3 mM CuSO$_4$ was favourable for the formation of copper nanoparticles it takes 1 h. The optimization study shows a significant effect on the synthesis of copper nanoparticles and the higher centralization of metal arrangement recommends the total of nanoparticles [26]. The development of copper nanoparticles increases with in temperature by utilizing the leaf concentrate of *G. seratta*. The absorbance band was expanded and situated at 341 nm and 345 nm at thermostat and microwave technique, separately (Fig. 6). At high temperature the decrease was supported because of the utilization of copper particle in the arrangement of cores. Finally, it was concluded that the optimum temperature was depend on the methods we adopt for the synthesis of nanoparticles [27].
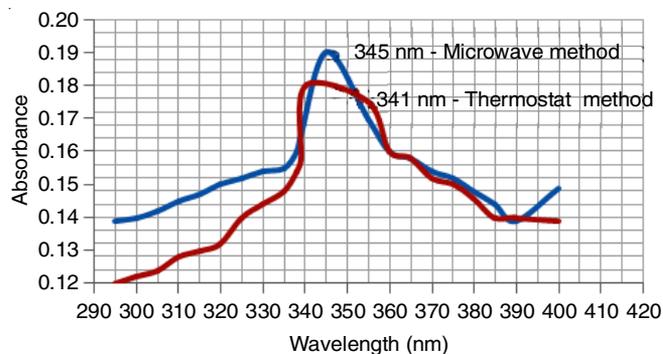


Fig. 6. UV-visible spectra of *G. serrata* mediated CuNPs

**FTIR analysis:** The functional group analysis was carried out using FTIR the band appear at 3431.41 cm$^{-1}$ present in *G. serrata* shifted to 3329.14 cm$^{-1}$ confirms the presence of phenolic –OH group, the band at 1633.61 cm$^{-1}$ in *G. serrata* is shifted 1637.56 cm$^{-1}$ confirms the presence of C=O group and the band at 671.11 cm$^{-1}$ present in *G. serrata* is shifted to 640.37 cm$^{-1}$ confirms the presence of aromatic ring. An analysis of the FTIR spectra of the extract and the synthesized CuNPs revealed that the copper nanoparticles might be surrounded by molecules like polyphenols, reducing sugars

and flavonoids, which are commonly found in plant extracts. These chemical constituents present in the leaf extract are capable of converting copper sulphate to copper nanoparticles due to their capping and reducing capacities. From these observations it is clear that the phytochemicals present in *G. serrata* leaf extract are responsible for reduction and stabilization by capping of CuNPs.

## Conclusion

The present study revealed that the potential efficiency of *G. serrata* was an efficient corrosion inhibitor as well as an efficient reductant. The *G. serrata* acts as anodic type inhibitor, which retards active passage of corrosion by forming a thin film formed on the surface which was confirmed through surface analysis. The *G. serrata* was also served as an efficient reducing agent for the synthesis of copper nanoparticles. Two methods were adopted for the synthesis, in that microwave method is preferred due to its time consuming and easiness. The *G. serrata* was used as a reducing as well as a stabilizing agent, which was confirmed through FTIR analysis.

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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